

APPENDIX I.

APPLICATION SITE AIR SAMPLE ANALYSIS OF NALED AND DICHLORVOS

Application Site Air Sample Analysis of Naled and Dichlorvos
Progress Report

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ABSTRACT

Application site air samples from seven periods of air sampling for naled and its transformation product, dichlorvos, were analyzed using a method developed by Environmental Toxicology's Trace Analytical Laboratory personnel. Maximum air concentrations of naled and dichlorvos during the application period and immediately following were 30.7 $\mu\text{g}/\text{sample}$ and 2.5 $\mu\text{g}/\text{sample}$, respectively. Maximum naled concentrations of 41.1 $\mu\text{g}/\text{sample}$ were found during period six. Dichlorvos concentrations ranged from the limit of quantitation (0.030 $\mu\text{g}/\text{sample}$) to a maximum of 20 $\mu\text{g}/\text{sample}$, also during the sixth period.

Several samples that gave analytical responses for naled and dichlorvos were confirmed, both quantitatively and qualitatively, using a mass selective detector (MSD), and qualitatively by fourier transform infrared (FTIR) gas chromatography.

Validation samples, fortified XAD-4[®] resin samples at levels of 0.25, 2.5 and 20 μg each, gave an overall recovery of 107% for both naled and dichlorvos. Air Resources Board's Quality Assurance Unit fortified XAD-4[®] resin samples had a 102 percent recovery for both naled and dichlorvos.

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INTRODUCTION

Due to the Proposition 65 implication of dichlorvos, this detailed interim application site air sampling report was prepared by Environmental Toxicology personnel to provide the Air Resources Board Personnel with pertinent information and alert them to possible issues that might exist from the results of the air sample analyses.

This report covers the second phase, analysis of application site air samples. The first phase, air sampling and trapping efficiencies of XAD-4[®] resin and analysis, was reported on in Spring 1995 (Reference 1).

Application site air samples were collected and shipped to the Department of Environmental Toxicology (Et Tox) at UC Davis by Air Resources Board (ARB) personnel. Two shipments of samples, along with the chain of custody, were received by Et Tox's Trace Analytical Laboratory (TAL) personnel. All samples were stored at -20 °C until the time of extraction and analysis. Extraction and sample work up was completed on 6/10/95. A complete historical perspective for this report is given in Appendix C.

The application site analytical samples were augmented with a set of quality assurance samples, prepared by ARB's quality assurance unit. These samples were delivered to TAL personnel prior to the start of the application sampling, and analyzed after completion of the application site samples.

ANALYSIS

Standard Preparation

Fresh analytical (gas chromatographic and fortification) standards were prepared from stock solutions of naled and dichlorvos (Appendix B). All neat analytical standards were stored at -20 °C and solutions were stored at 4 °C, until the time of use.

Extraction/Workup

The method used for the analysis of naled and dichlorvos was devised by Environmental Toxicology personnel and reported elsewhere (Appendix A, Reference 1). Essentially the method consists of adding ethyl acetate to the samples and mechanically swirling the samples for one hour and analyzing an aliquot. Approximately 50 percent of the samples did not require concentration, due to the sensitivity of the analysis and the concentration of dichlorvos and naled in the samples.

While the original method included the use of a silica column for clean up, the current samples did not require further clean up due to the high concentration of naled and dichlorvos and the chosen parameters of the analytical system.

Instrumentation

A Hewlett Packard 5890A gas chromatograph equipped with a N/P detector and a HP 7673 Autosampler was used for the analysis. The bead voltage was adjusted so that a 3 μ l injection of a 0.005 ng/ μ l standard produced a peak height greater than the limit of quantitation (LOQ) (See Quantitation). Peak quantitation accomplished via a TurboChrom[®] data station (Perkin Elmer) into an IBM[®] PC where the peaks were integrated and the results were entered into an EXCEL[®] (Microsoft) spreadsheet program. A wide bore capillary column (0.53 mm) was utilized in the analysis. The analysis was optimized for high sensitivity to preclude loss of dichlorvos during concentration due to its high vapor pressure. Parameters for the analytical instrumentation are listed in Table 1.

Quantitation

Analysis of samples was quantified by using a 5-point external linear regression standard curve for naled and dichlorvos that ranged from a maximum of 0.080 ng/ μ l to a minimum of 0.005 ng/ μ l. Each sample was injected twice and standard(s) were interdispersed between samples during each analysis (set). The average of both analyses were reported. The LOQ of 0.030 μ g/sample was based on the lowest point of the standard curve (0.005 ng/ μ l injected), the minimal sample volume that the sample was concentrated to (3.0 ml) and a multiplication factor of 2 (only one half of the sample was used). The LOQ was at least five times above the limit of detection (LOD) of the detector. The LOD was at least three times the noise of the detector.

Table 1. Gas Chromatograph Instrument Parameters used for Analysis

Instrument	Injector	Detector (°C)	Temperature Column (°C)				Column
			Initial	Rate	Final	Hold (Min)	
HP-5890	250	280	100	20	220	0.5	30 m x 0.53 mm XTI-5 ¹ @ 20 ml/min

1: Restek Inc.

Quality Assurance

While it was not a requirement to follow strict Good Laboratory Practices (GLP) guidelines, quality assurance was kept at a maximum to keep the integrity of the project. Controls, (checks, blanks) and fortifications (validation samples), three replicates of control resin fortified with 0.25 µg each naled and dichlorvos, were run with every set. Documentation for the project was at a maximum, including the use of notebooks, instrument logbooks and/or computer spreadsheets. All of the necessary components were in place to assure that the study would be reconstructible, a prime requisite for a GLP study.

Validation spikes, spiked at three levels consisting of 0.25, 2.5, and 20 µg each of naled and dichlorvos was spiked, in triplicate, directly onto the XAD-4[®] resin, and was carried through the method scheme along with the extraction of the samples (Table 4, Results Section). The higher levels were done to cover the range of residues found in the samples.

On June 2, 1995 ARB Personnel delivered 22 resin fortified quality assurance samples to TAL for analysis. All of these resin spikes samples were analyzed within 72 hours of the application sample analysis. The procedures used for work up and analysis was exactly the same as used for the application site samples. The results of these samples are listed in Table 5 of the results section of this report.

Confirmation

Several samples, which gave a positive response for the nitrogen-phosphorus detector, and had the same retention time as naled and dichlorvos, were submitted for confirmation using a Hewlett Packard 5971A Mass Selective Detector (MSD), that was operated in the Selective Ion Monitoring mode (SIM), using ions 109, 185 and 220 for confirming the presence of naled and dichlorvos in samples. The column was a 10 m X 0.25 mm DB - 5 narrow bore fused silica capillary column (J & W Scientific) that was operated at an initial temperature of 100 for 2 minutes and ramped to 160 at 10 °C/min and then ramped to 250 °C at 20 °C/min. The criteria used for confirmation was retention time with naled

and dichlorvos standard comparison. Several samples were quantitated as well, using the MSD with the same standards used for the analytical method as a comparison. Because the spectra of dichlorvos and naled has ions that are common to a vast number of compounds, several samples were run in scan mode and complete spectra were obtained and compared with spectra from the library as a means of confirmation (Appendix D).

Further confirmation was accomplished by using a Hewlett Packard model 5965A infrared detector coupled to a Hewlett Packard model 5980A gas chromatograph. Several samples including standards were concentrated and injected. The Instrument conditions are given in Table 2. Spectra were obtained for both the standards and samples, for naled and dichlorvos. These spectra were compared with standard library spectra, which the data system pick from a library of 535 spectra (Appendix E).

Table 2. Gas Chromatograph Instrument Parameters used for FTIR Analysis

Instrument	Temperature Column (°C)						Column
	Injector (°C)	Detector Initial	Rate	Final	Hold (Min)		
HP-5890	250	275	100	10	250	10	25 m x 0.32 mm HP-5 ¹

1: Hewlett Packard, Inc..

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RESULTS

Analytical Results

Table 3 contains the number of micrograms of naled and dichlorvos found in each sample. Also included is the equivalent amount of naled that was transformed into dichlorvos (a), and the equivalent total number of micrograms of naled per sample for each period at each site (b). The highest concentration of naled, 41.1 $\mu\text{g}/\text{sample}$, was during period 6 at the north site. The total combined mass of naled, the equivalent amount of naled that was transformed to dichlorvos, plus the naled mass, was 75.0 $\mu\text{g}/\text{sample}$. The next highest mass of naled, 30.8 $\mu\text{g}/\text{sample}$, was at the north site during and immediately following application.

Table 4. and Figure 1 contains the equivalent amount of naled mass for each sampling site and period. The highest total mass for the application period was 35.0 μg at site N, and the highest total mass for all periods was 75.0 μg also at site N during the sixth period. Figure 2 gives a three dimensional representation of the total naled mass/sample, period and site. Note that elapsed time per period may vary greatly (data concerning actual elapsed time per period was not available at the time of writing).

Table 3. Analytical Results for Naled and Dichlorvos

Log #	Sample ID	Dichlorvos		Dichlorvos	
		found (ug)	found (ug)	Equivalent as	Total
			Naled	Naled (a)	Naled (b)
Log 1	0 S	<0.030	< 0.030	<0.052	< 0.082
Log 2	0 E1	< 0.030	< 0.030	<0.052	< 0.082
Log 3	0 E2	< 0.030	< 0.030	<0.052	< 0.082
Log 4	0 N	< 0.030	< 0.030	<0.052	< 0.082
Log 5	0 W	< 0.030	< 0.030	<0.052	< 0.082
Log 6	1 S	Trace	0.231	<0.052	0.23
Log 7	1 E1	2.10	15.48	3.60	19.08
Log 8	1 E2	1.99	14.51	3.42	17.92
Log 9	1 N	2.48	30.75	4.26	35.01
Log 10	1 W	0.64	6.12	1.09	7.21
Log 11	2 S	Trace	0.106	<0.052	0.11
Log 12	2 E1	0.14	0.53	0.23	0.77
Log 13	2 E2	0.17	0.69	0.29	0.98
Log 14	2 N	0.23	1.38	0.40	1.78
Log 15	2 W	Trace	0.134	<0.052	0.13
Log 16	BLANK	<0.030	< 0.030	<0.052	<0.082
Log 17	3 S	0.082	0.32	0.14	0.46
Log 18	3 E1	0.17	0.48	0.29	0.76
Log 19	3 E2	0.15	0.46	0.26	0.72
Log 20*	3 N	0.11	0.36	0.19	0.55
Log 21	3 W	< 0.030	0.043	<0.052	0.04
Log 22	4 S	0.050	0.15	0.086	0.23
Log 23	4 E1	0.050	0.15	0.086	0.23
Log 24	4 E2	Trace	0.075	<0.052	0.08
Log 25	4 N	Trace	0.10	<0.052	0.10
Log 26	4 W	< 0.030	< 0.030	<0.052	<0.082
Log 27	5 S	2.60	4.59	4.46	9.05
Log 28	5 E1	0.60	1.15	1.03	2.18
Log 29	5 E2	0.63	1.14	1.08	2.22
Log 30	5 N	7.68	20.21	13.20	33.41
Log 31	5 W	3.25	8.82	5.58	14.40
Log 32	6 S	18.04	22.22	31.02	53.24
Log 33	6 E1	1.891	3.300	3.25	6.55
Log 34	6 E2	1.933	3.519	3.32	6.84
Log 35	6 N	19.69	41.11	33.86	74.97
Log 36	6 W	19.98	20.28	34.35	54.63
Log 37	7 S	1.94	2.12	3.33	5.45
Log 38	7 E1	0.32	0.36	0.55	0.91
Log 39	7 E2	0.33	0.37	0.57	0.95
Log 40	7 N	4.87	5.28	8.38	13.66
Log 41	7 W	2.33	3.12	4.01	7.13

Table 4. Equivalent Naled Mass for Each Site and Period ($\mu\text{g}/\text{Sample}$).

Sampling Period	Total Naled at the Application Site				
	E	S	W	N	Total
0	<0.082	< 0.082	< 0.082	< 0.082	<0.082
1	18.5	0.231	7.21	35.0	61.0
2	0.872	0.106	0.134	1.78	2.89
3	0.740	0.462	0.043	0.548	1.79
4	0.153	0.232	<0.082	0.103	0.488
5	2.20	9.05	14.4	33.4	59.1
6	6.70	53.2	54.6	75.0	190
7	0.930	5.45	7.13	13.7	27.2

Figure 1. Naled mass for each site and period of sampling

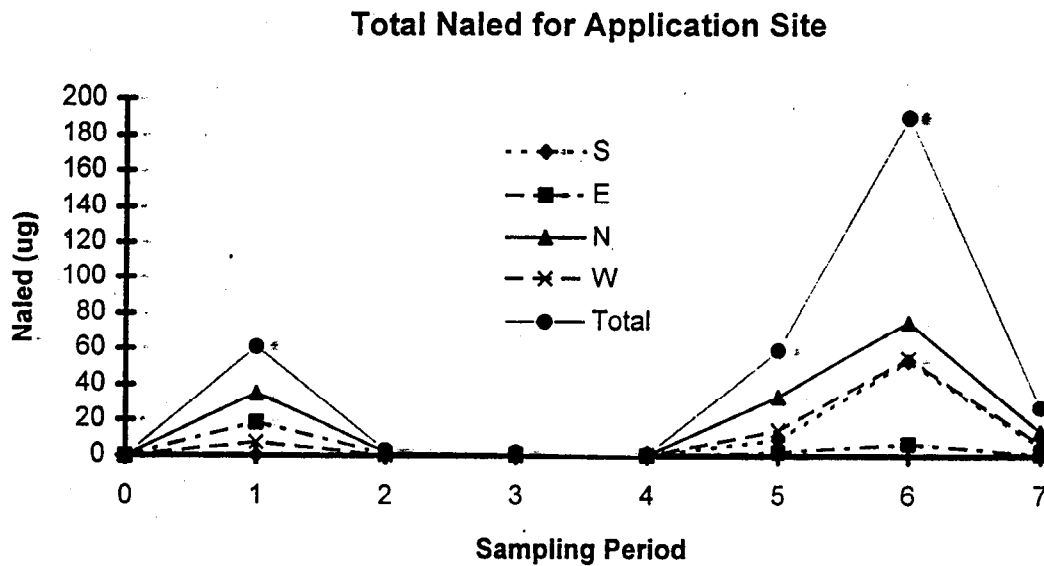


Figure 2. Total Naled for Application Site

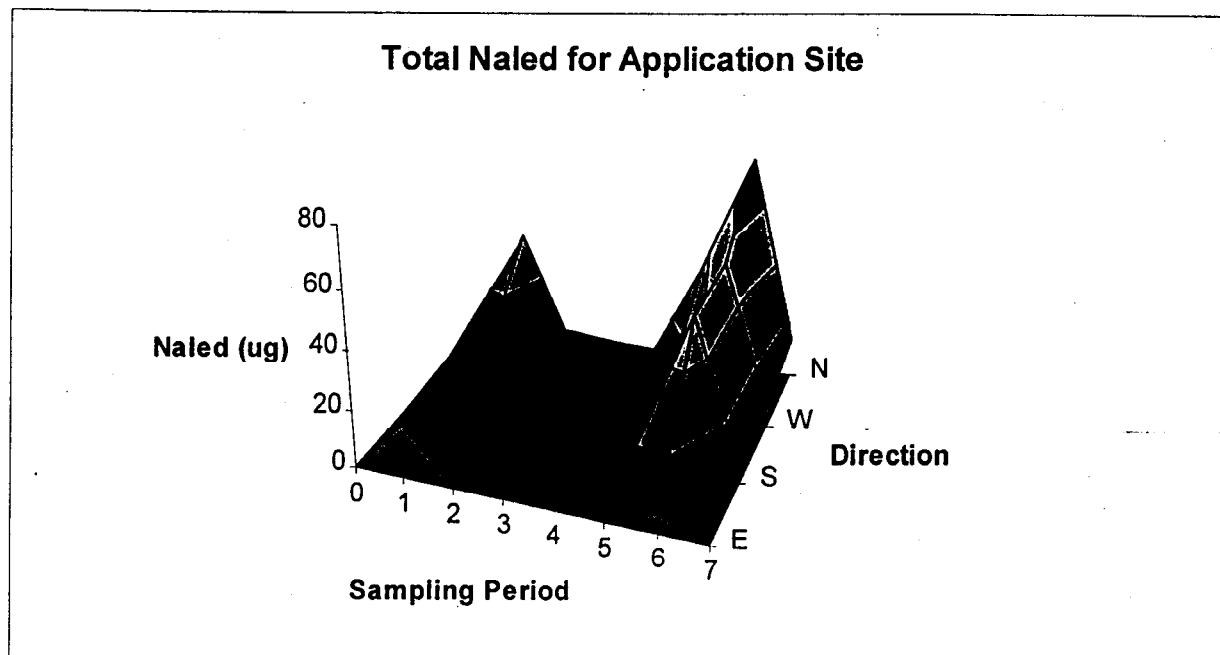
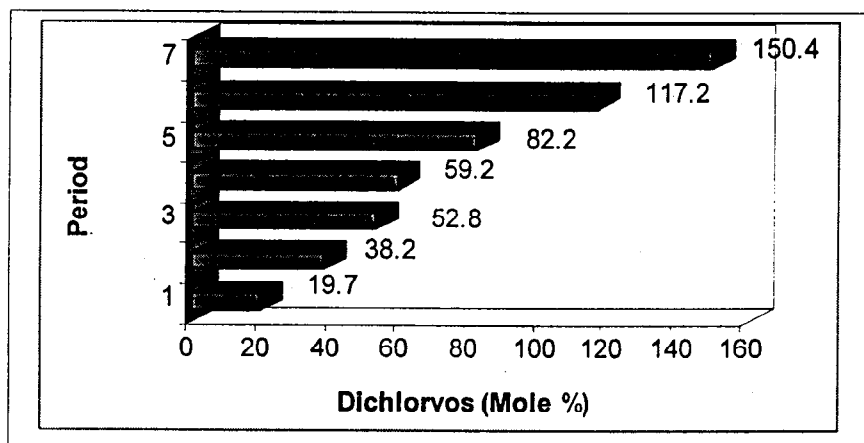


Figure 3. Percent of Naled as Dichlorvos on a Mole Basis



Validation Spikes

The percent recoveries for naled ranged from 83% to 124% and for dichlorvos the recoveries ranged 95% to 116%. While the recoveries for both compounds were higher than anticipated, they were well within the range of acceptable criteria for residue recovery data. Table 5 gives the amount spiked, average for each spike level and the standard deviation for the level.

Table 5. Validation Samples Recoveries

Sample Id	Amount Spiked (μ g)	Dichlorvos			Naled		
		Recovery (%)	Average(%)	Std Dev.	Recovery (%)	Average(%)	Std Dev
V-R-1 (0.25)	0.25	105			108		
V-R-2 (0.25)	0.25	116			124		
V-R-3 (0.25)	0.25	111	111	5.4	116	116	7.60
V-R-1 (2.5)	2.5	104			107		
V-R-2 (2.5)	2.5	116			111		
V-R-3 (2.5)	2.5	110	110	5.68	111	110	2.31
V-R-1 (20)	20	102			99		
V-R-2 (20)	20	105			101		
V-R-3 (20)	20	95	101	4.89	83	95	9.85

ARB Quality Assurance Samples

The results of the ARB quality assurance samples are listed in Table 6. In general, the analysis results are in good agreement with ARB's assigned values for both dichlorvos and naled. The average percent difference between TAL's reported value ARB's for dichlorvos was 102% with a standard deviation of 8.2 %. The average difference for naled was 102% with a standard deviation of 5.2%. These values are in excellent agreement when taking into consideration the variability of the method and, for dichlorvos, the high vapor pressure of the compound.

Table 6. ARB Quality Assurance Spike Results

Sample ID	TAL Results		ARB Assigned Values (µg)		% of Assigned		% of Assigned	
	Dichlorvos µg/Sample	Naled µg/Sample	Dichlorvos	Naled	Dichlorvos Difference	%	Naled Difference	%
Nal-1	0.56	<0.03	0.63	0.00	90.0	10.0		
Nal-2	<0.03	0.53	0.00	0.50			106	-6.0
Nal-3	2.54	<0.03	2.50	0.00	101	-1.40		
Nal-4	0.22	<0.03	0.25	0.00	87.6	12.4		
Nal-5	0.04	1.31	0.00	1.25			105	-5.0
Nal-6	0.26	0.49	0.25	0.50	106	-5.60	97.8	2.2
Nal-7	1.42	4.81	1.25	5.00	113	-13.2	96.1	3.9
Nal-8	0.09	2.55	0.00	2.50			102	-2.0
Nal-9	0.61	1.24	0.63	1.25	96.7	3.33	99.1	0.88
Nal-10	0.25	<0.03	0.25	0.00	98.0	2.0		
Nal-11	1.48	4.79	1.25	5.00	118	-18	95.7	4.3
Nal-12	0.62	<0.03	0.63	0.00	98.6	1.43		
Nal-13	<0.03	0.47	0.00	0.50			94.8	5.2
Nal-14	0.26	0.49	0.25	0.50	106	-5.6	98.0	2.0
Nal-15	0.05	1.38	0.00	1.25			111	-11
Nal-16	0.64	1.36	0.63	1.25	101	-0.95	109	-9.1
Nal-17	0.08	2.67	0.00	2.50			107	-6.6
Nal-18	<0.03	<0.03	0.00	0.00				
Nal-19	0.27	<0.03	0.25	0.00	106	-6.0		
Nal-20	0.27	0.52	0.25	0.50	108	-7.6	104	-3.6
Nal-21	2.55	<0.03	2.50	0.00	102	-2.0		
Nal-22	0.06	1.32	0.00	1.25			106	-5.8

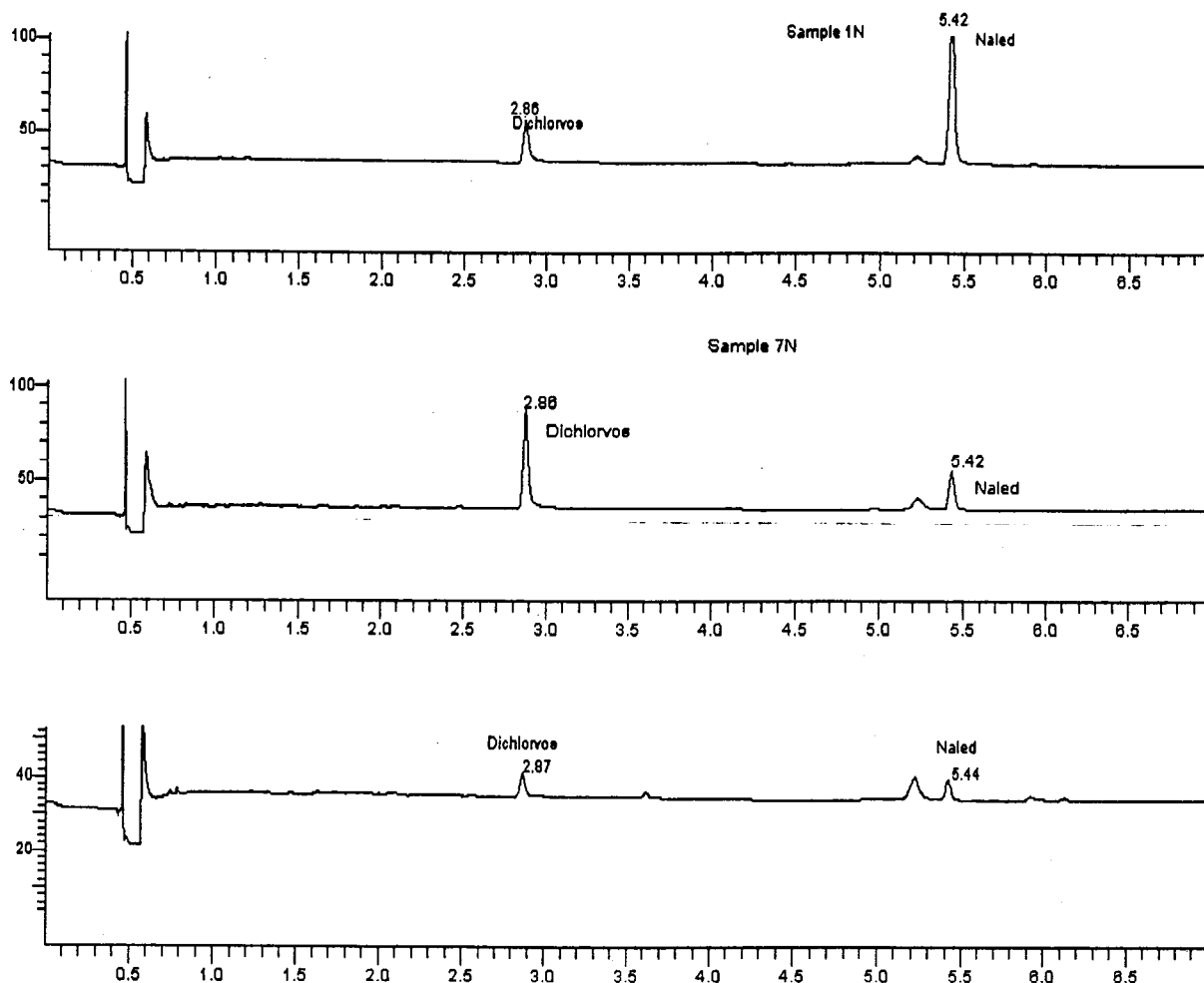


Figure 4. Sample Chromatograms. Top Sample 1N during application, Middle: sample 7N, Bottom: 10 pg/ul injection of naled (Rt = 5.44 min) and dichlorvos (Rt = 2.87 min).

The percent of naled that was detected as dichlorvos was converted to equivalent moles naled and calculated on a percent of the naled detected for that period. Figure Three gives the average percent for each site for each period on a mole basis. Only approximately 20 percent of the total detected for period one was dichlorvos while for period seven the amount of dichlorvos was 150 percent of amount of naled detected.

CONCLUSIONS

There is an increase of dichlorvos with time following a naled application. The exact air concentration could not be measured because of the lack of data for calculating how much air was processed by each air sampler. However, there appears to be significant amount of naled that is transformed to dichlorvos. Thio organophosphates have been known to be converted to their corresponding oxons, when the parent compound is spiked directly on resin, and air is pulled through the resin for an extended period of time (Reference 2). However, there was no conversion of naled to dichlorvos when naled was applied directly to resin and air passed for a 24 hour period (Reference 1). Therefore, the presence of dichlorvos in the samples must be because of conversion of naled due to soil pH, soil moisture, photolysis and/or microbial degradation.

Because dichlorvos has potential proposition 65 issues associated with it, several items should be included in field work. First of all, no two applications are exactly the same. For example, there may be higher soil moisture, clouds, or some other parameter that will influence the volatility of the compounds of interest. The following items are listed as suggestions because no applications are the same:

1. On site micro meteorological instrumentation including wind speed and direction, temperature, humidity and solar radiation. Meteorological data will have a large influence on the application results. Also, if there is a chance of rain, a tipping bucket rain gauge should be part of the system.
2. The amount of soil moisture has a direct effect on the amount of a chemical's volatilization from soil. Capillary action of water evaporating near the surface of the soil will cause a "bloom" of pesticide into the air. Therefore, soil moisture readings are also encouraged along with soil heat flux.
3. The type of field, bare soil vs. grass vs. orchard etc. will also influence the volatility of the compound. For example, there is a gas exchange for turf areas that will increase the amount of volatility over bare soil. Soil type (sand, clay etc.) will have an effect on the environmental parameters affecting the air concentration.
4. The total area applied along with the application type (ground rig or aerial) and the amount of active ingredient (in pound per acre) should also be recorded. In addition the above, application duration as well as any problems that might have arisen during the application (i.e. application rig broke down and was inoperable for 2.5 hours).
5. A "tank sample" should be submitted for analysis to screen for the correct concentration and check for potential breakdown products.
6. The use of a "marker compound" should be considered for all application sites. It may

be possible to "normalize" on the marker compound and compare applications. Environmental Toxicology personnel (Seiber, Majewski and McChesney) have used this approach for both down wind air sampling and aerodynamic flux measurements. The compound of choice, was diazinon, an organophosphate of medium volatility.

7. Air sample distance, from the edge of the field to the sampling cup, should be accurately recorded. Furthermore, two sets of samples should be placed on the downwind side of the field; one near the edge and one further away to check for dilution of air concentration with distance from the field.

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2. M. M. McChesney, personal communication

APPENDIX

Appendix A: Method of Analysis for Naled and Dichlorvos

ARB Project 1995

Naled/Dichlorvos Sample Preparation

Add 75 ml of ethyl acetate directly to wide mouth sampling jar containing the resin. Placed sample on rotating platform for at least 1 hour. One-half (37.5 ml) of the sample was measured out using a 50 ml graduated cylinder into a 250 ml round bottom flask. The sample was concentrated* just to dryness and transferred to a graduated screw-top centrifuge tube and brought to 3 ml (equivalent to 6 ml for total sample). The sample was injected on GC/NPD for analysis.

*Note: If necessary, samples with large residues were diluted directly from the original sample for analysis.

Concurrent validations were also prepared by adding the appropriate amount of standard directly to unused resin in a wide-mouth jar and handled exactly as a normal sample.

For 0.125 μ g of naled/dichlorvos, 250 μ l of solution "G" (2 μ g/ml Naled/Dichlorvos) was added using a 250 μ l Hamilton syringe.

For 2.5 μ g of naled/dichlorvos, 1250 μ l of solution "G" (2 μ g/ml Naled/Dichlorvos) was added using a 500 μ l Hamilton syringe (2-1/2 times).

For 20 μ g of naled/dichlorvos, 20 μ l of each of the stock solutions (1.00 mg/ml) was added using a 25 μ l Hamilton syringe.

Appendix B: Preparation of Naled (Dibrom) and Dichlorvos Standards, 6/10/95

Received from: Chem Service, Inc
 Received Date: 5/18/95
 Item: **Dibrom** Analytical Standard
 (Naled/1,2-Dibromo-2,2-dichloroethyl dimethyl phosphate)
 CAS Number: 300-76-5
 P.O.# DOV023C17
 Catalog# PS-605
 Lot # 146-103B
 Assay: 98.0%
 Expiration Date: 4/99
 Storage Conditions: Refrigerate, store under nitrogen
 Quantity Shipped: 1.0 gm

Naled Stock Standard $(7.9637 - 7.8617) = 0.1020$ gm

1.00 mg/ml Naled Stock = $(102.0 \text{ mg} \times 0.980)/100\text{ml}$ in ethyl acetate

Dilutions The following dilute standards were made on 6/10/95 by CRM

- "A" -- 1.0 ml Dichlorvos Stock in 10 ml for final concentration $100\mu\text{g/ml}$
- "B" -- 1.0 ml Naled Stock in 10 ml for final concentration $100\mu\text{g/ml}$
- "C" -- $500\mu\text{l}$ of Dichlorvos Stock in 50 ml for final concentration $10\mu\text{g/ml}$
- "D" -- $500\mu\text{l}$ of Naled Stock in 50 ml for final concentration $10\mu\text{g/ml}$
- "E" -- $50\mu\text{l}$ of Dichlorvos Stock in 50 ml for final conc of $1.0\mu\text{g/ml}$
- "F" -- $50\mu\text{l}$ of Naled Stock in 50 ml for final conc of $1.0\mu\text{g/ml}$
- "G" -- $200\mu\text{l}$ of Dichlorvos and Naled Stocks into 100 ml for final conc of $2.0\mu\text{g/ml}$ each

*Note: Dichlorvos stock was made on 5/8/95

GC Standards Preparation

Conc. Wanted	Total Volume	conc. naled + dichlorvos μl used	stock std
80 $\text{pg}/\mu\text{l}$	25ml	200	10 $\mu\text{g/ml}$
40	50 ml	200	10 $\mu\text{g/ml}$
20	100ml	200	10 $\mu\text{g/ml}$
10	200ml	200	10 $\mu\text{g/ml}$
5	400ml	200	10 $\mu\text{g/ml}$

Appendix C: Historical Perspective of the Application Phase of the Project

- 5/8/95 Preparation of Naled and Dichlorvos Stock Standards from analytical (see 1994 for receipt).
- 5/18/95 Received new Naled standard from Chem Service.
- 6/2/95 Received Quality Assurance Samples from ARB & placed in -20C freezer.
- 6/8/95 Received 36 site samples from Don Fitzell on dry ice.
- 6/9/95 Received final 6 site samples from Ken Lewis on dry ice.
- 6/10/95 Prepared new Naled stock solution. Prepared dilutions of stock standards (naled & dichlorvos), spiking and GC standards. Prepared 3 validation spikes @ 0.250µg Naled & Dichlorvos. Extracted and started sequence to analyze all 41 samples & 3 validations on HP5890_NPD_OI GC.
- 6/11/95 Removed excess standard injections on the part of the sequence which had not been run yet.
- 6/12/95 Prepared 3 validation samples (0.25µg each, R4,R5,R6) for QA samples. Extracted QA and validation samples. Split (½) of each sample. Also sub-sampled all QA samples from original solution to be analyzed on the HP5890_NPD_OI for scouting for appropriate dilutions. Diluted QA samples as appropriate. Started sequence to analyze all 22 QA & 3 validation samples.
- 6/13/95 Re-analyzed QA samples Nal-5,15,22.
- 6/14/95 Re-analyzed Nal-15 and R5 validation sample. Prepared Dichlorvos and Naled standard to check for impurity of Dichlorvos in Naled.
- 6/15-6/25 Confirmation work using mass selective and infrared detectors.
- 6/22/95 Re-sampled sample 3N (log) along with 3 validation samples (2.5µg each). Analyzed on HP5890/NPD.
- 6/23/95 Faxed QA results to Jane Pettit.
- 6/25/95 Prepared 3 validation samples (20µg each, R1,R2,R3). Extracted and injected on HP5890_NPD_OI.
- 6/28/95 Received preliminary QA results from Jane Pettit.

Appendix D: Confirmation of Naled and Dichlorvos Using Mass Selective Detector

Figure 5. MSD Scan Mode of Sample 6N and Resulting Spectra Comparison for Naled.

Figure 6. MSD Scan Mode of Sample 6N and Resulting Spectra Comparison for Dichlorvos

Appendix E: Confirmation of Naled and Dichlorvos using Fourier Transform Infrared Gas Chromatography. List of Chromatograms and Spectra

<u>Figure #</u>	<u>Chromatogram/Spectra</u>
Figure 7.	2 µl Injection of 100 ng/µl Dichlorvos Standard
Figure 8.	2 µl Injection of 100 ng/µl Naled Standard
Figure 9.	3 µl Injection of 2.5 µg Spiked XAD-4® Resin Validation Sample
Figure 10	3 µl Injection of Sample 6N., Naled Spectrum
Figure 11	3 µl Injection of Sample 6N., Dichlorvos Spectrum
Figure 12	3 µl Injection of Sample 1N., Naled Spectrum
Figure 13	3 µl Injection of Sample 1N., Dichlorvos Spectrum
Figure 14	3 µl Injection of 20 µg Spiked XAD-4® Resin Validation Sample, Naled Spectrum
Figure 15	3 µl Injection of 20 µg Spiked XAD-4® Resin Validation Sample, Dichlorvos Spectrum

Figure 5. MSD Scan of Sample 6N and Spectra Comparison for Naled

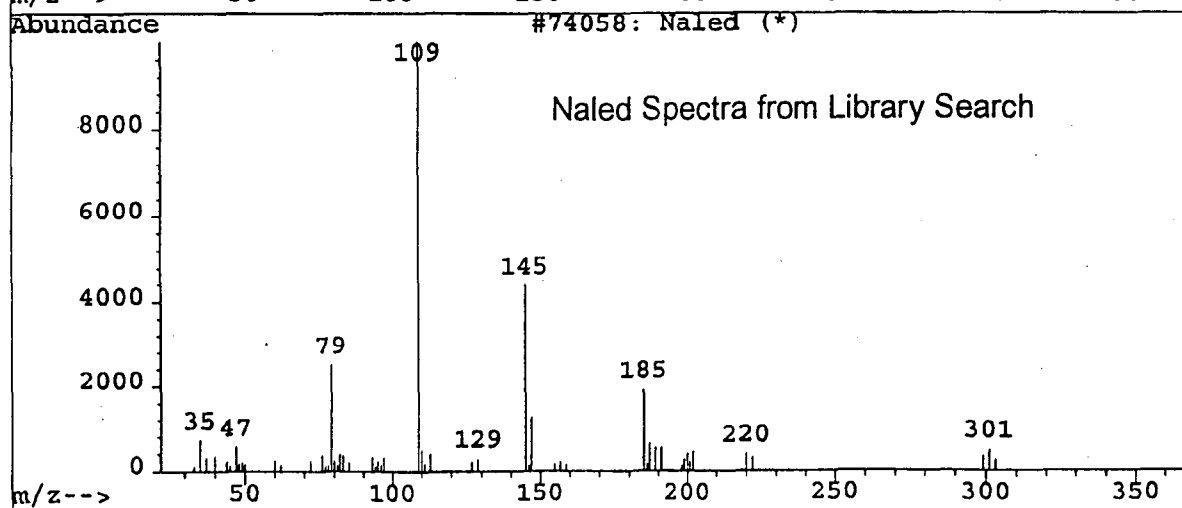
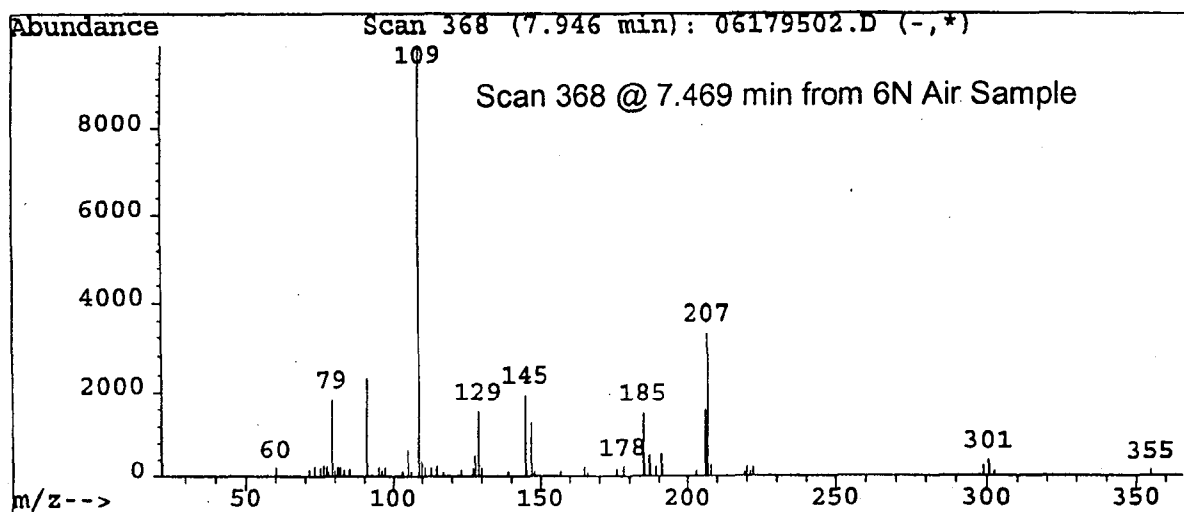
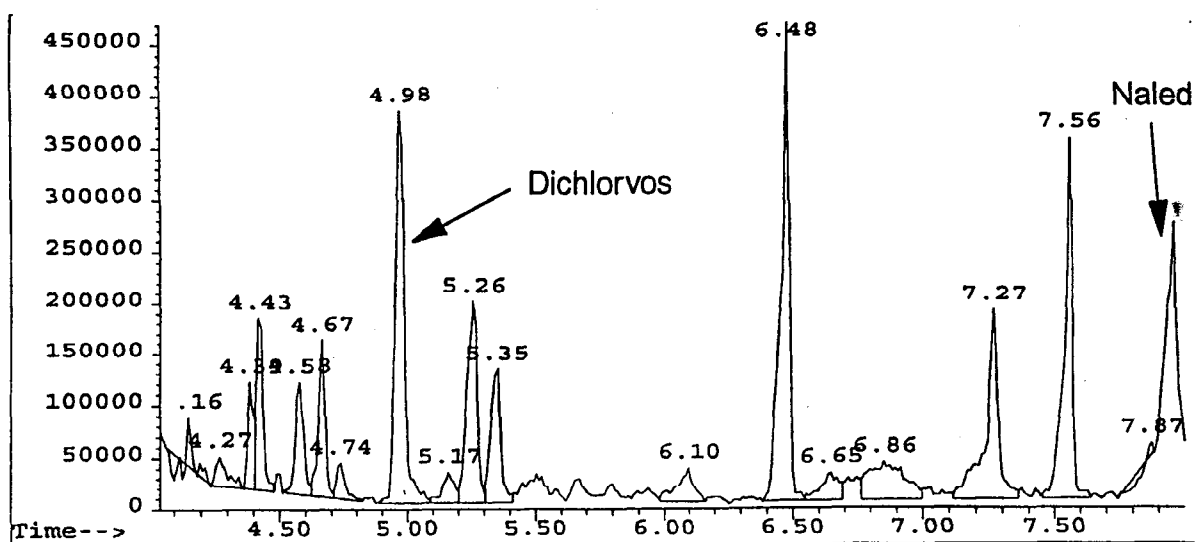


Figure 6. MSD Scan of Sample 6N and Spectra Comparison for Dichlorvos

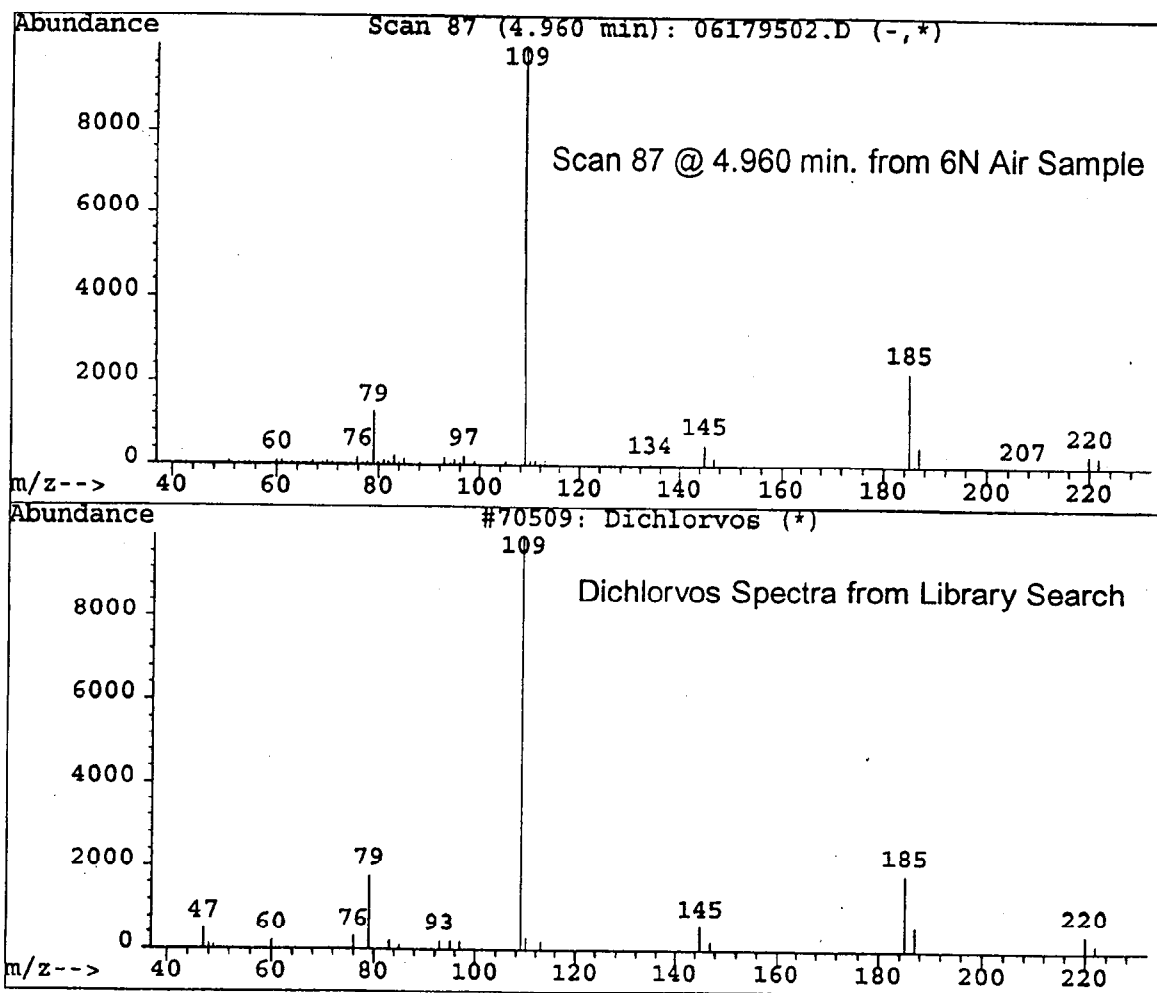
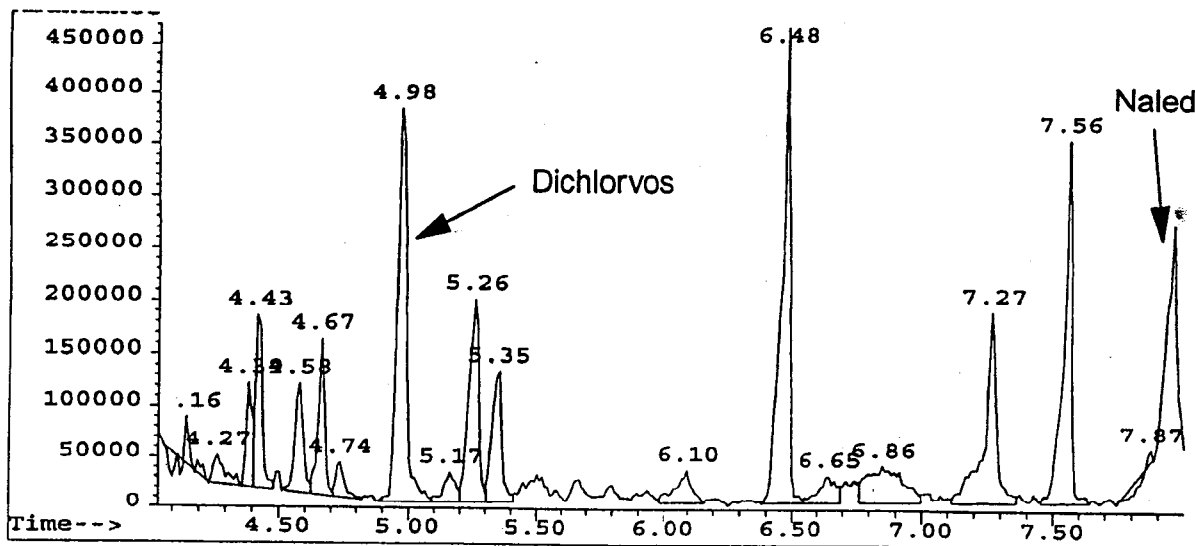
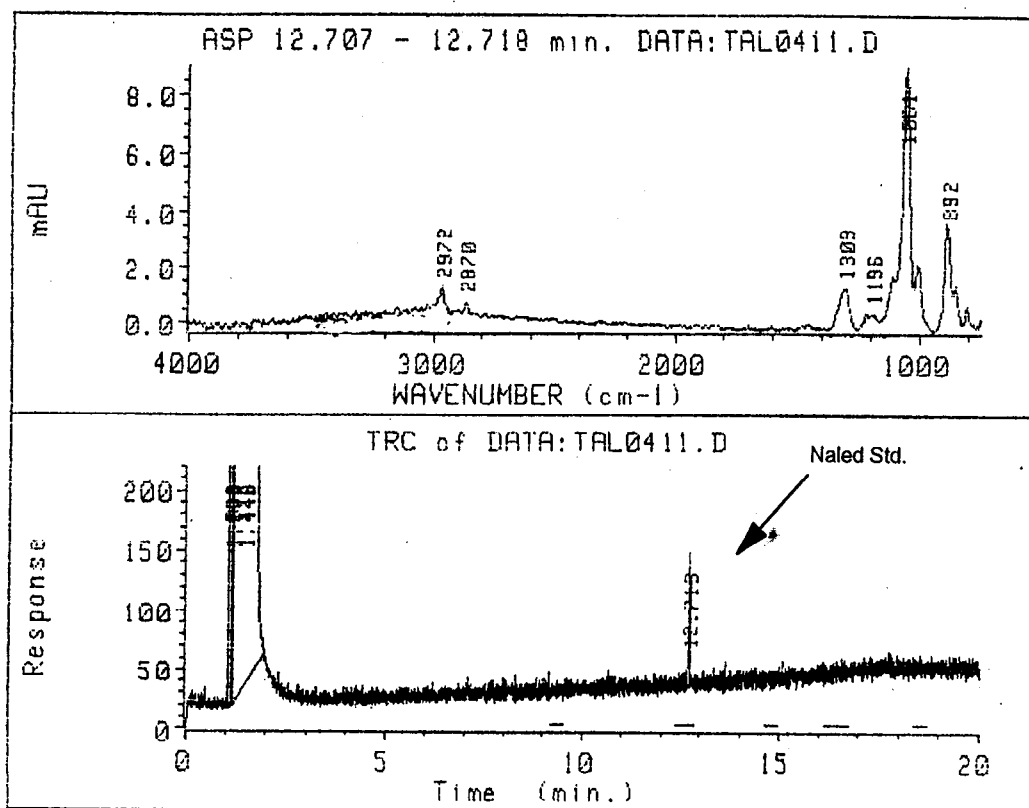
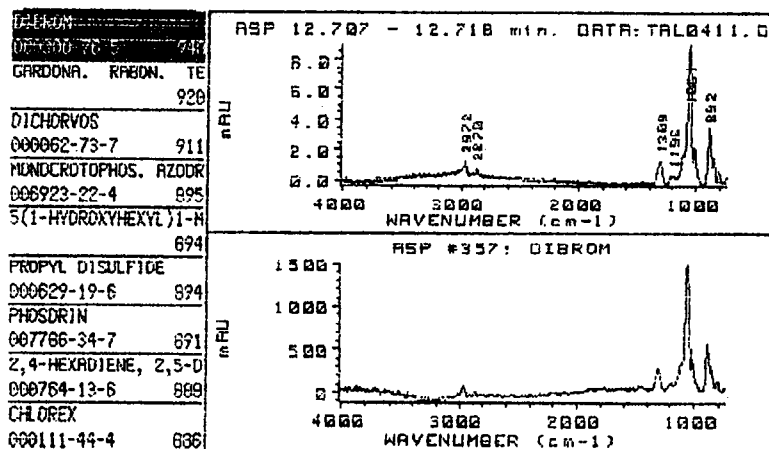


Figure 7. GC/FTIR Confirmation: 2 ul X 100 ng/ul Naled Standard



GRAPHICS RESULTS

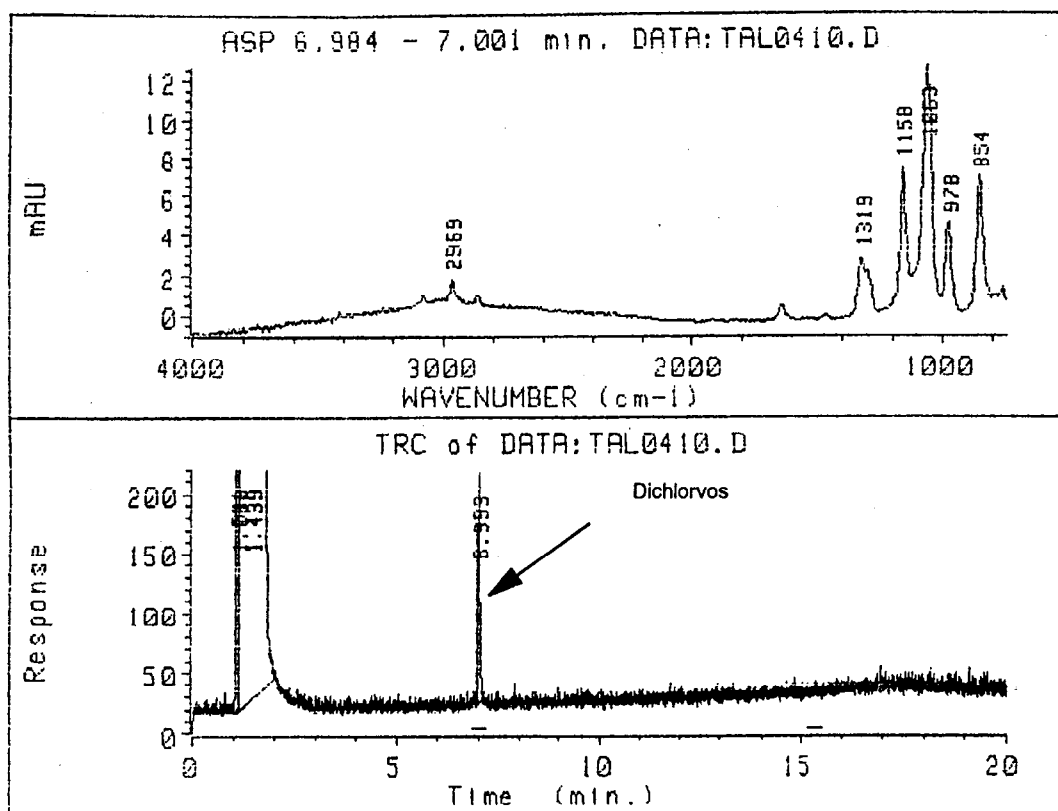
Version 1.0 25-Feb-87



← Infrared Spectra
from Naled Injected

← Infrared Spectra
from Library Search

Figure 8. GC/FTIR Confirmation: 2 ul X 100 ng/ul Dichlorvos Standard



GRAPHICS RESULTS

Version 1.0 25-Feb-87

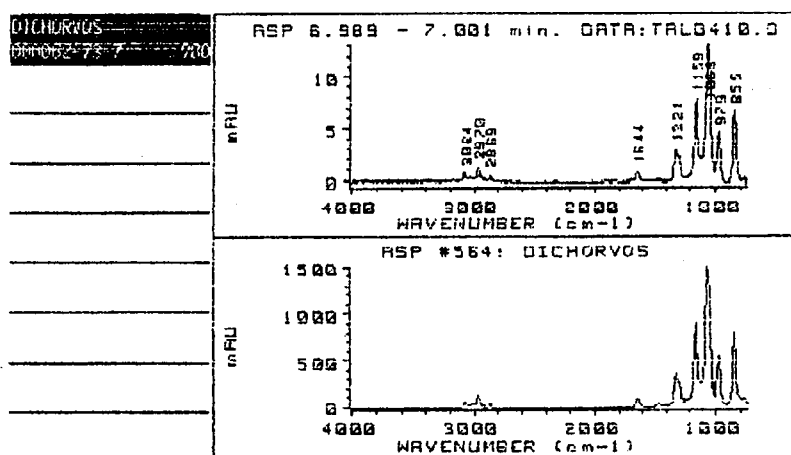
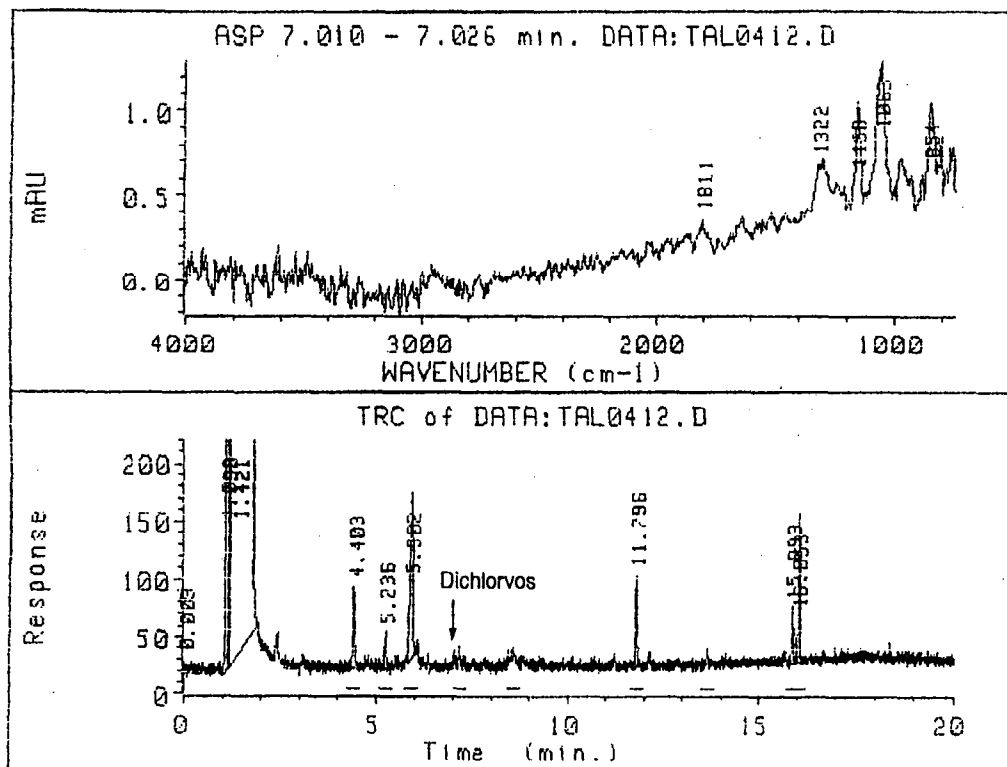
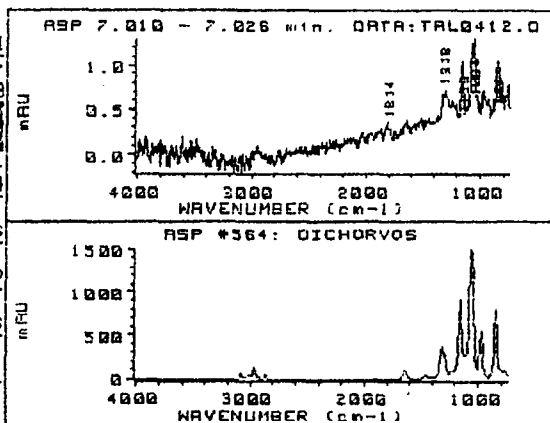
Infrared Spectrum
from Dichlorvos injectedInfrared Spectrum
from Library Search

Figure 9. 3 μ l Injection of 2.5 μ g Fortified XAD Resin Sample R-1

GRAPHICS RESULTS

Version 1.0 25-Feb-87

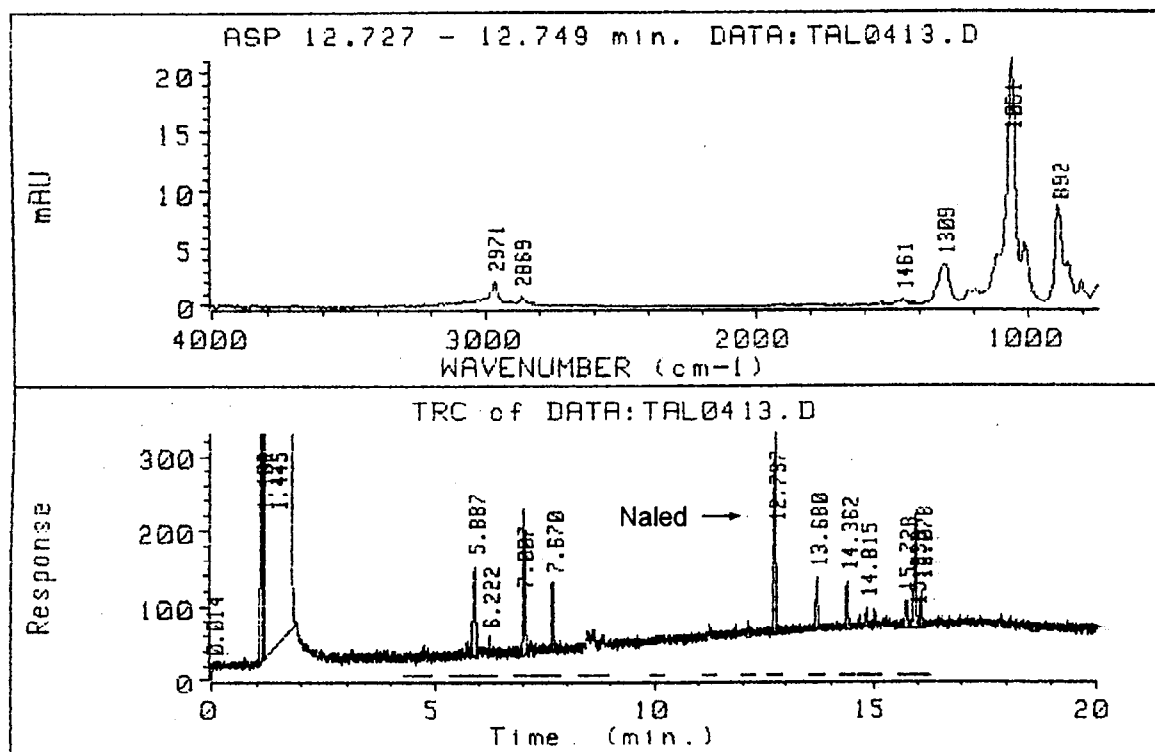
DICHLORVOS	
000062-73-7	811
D,O-DIETHYL-D-3,5,6-	
758	
NAIPHTHALENE, 1,3-DIM	
000575-81-7	742
NAIPHTHALENE, 1-ETHYL	
001127-76-0	744
THIODAN I	
000759-98-8	733
METHYL PARATHION	
729	
METHYL PARATHION	
000298-00-0	723
Z,6-DICHLOROHYDROQUI	
701	



← Infrared Spectrum
from Dichlorvos injected

← Infrared Spectrum
from Library Search

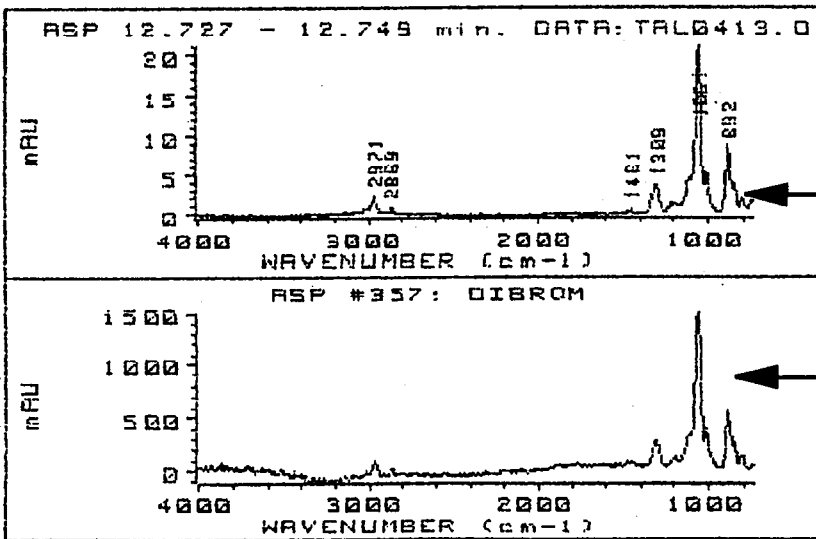
Figure 10. FTIR Confirmation: Log 35 - 6N, Naled



GRAPHICAL RESULTS

Version 1.0 23-Feb-87

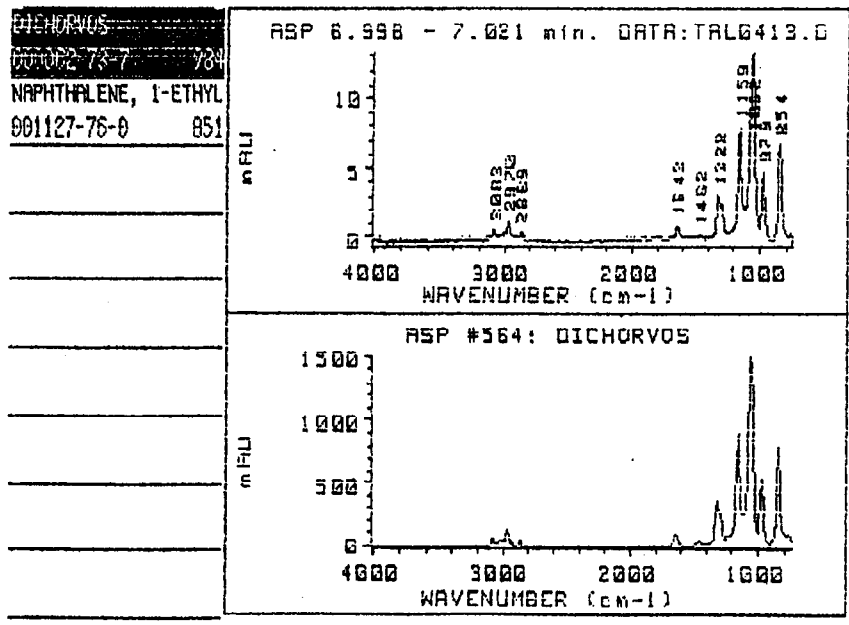
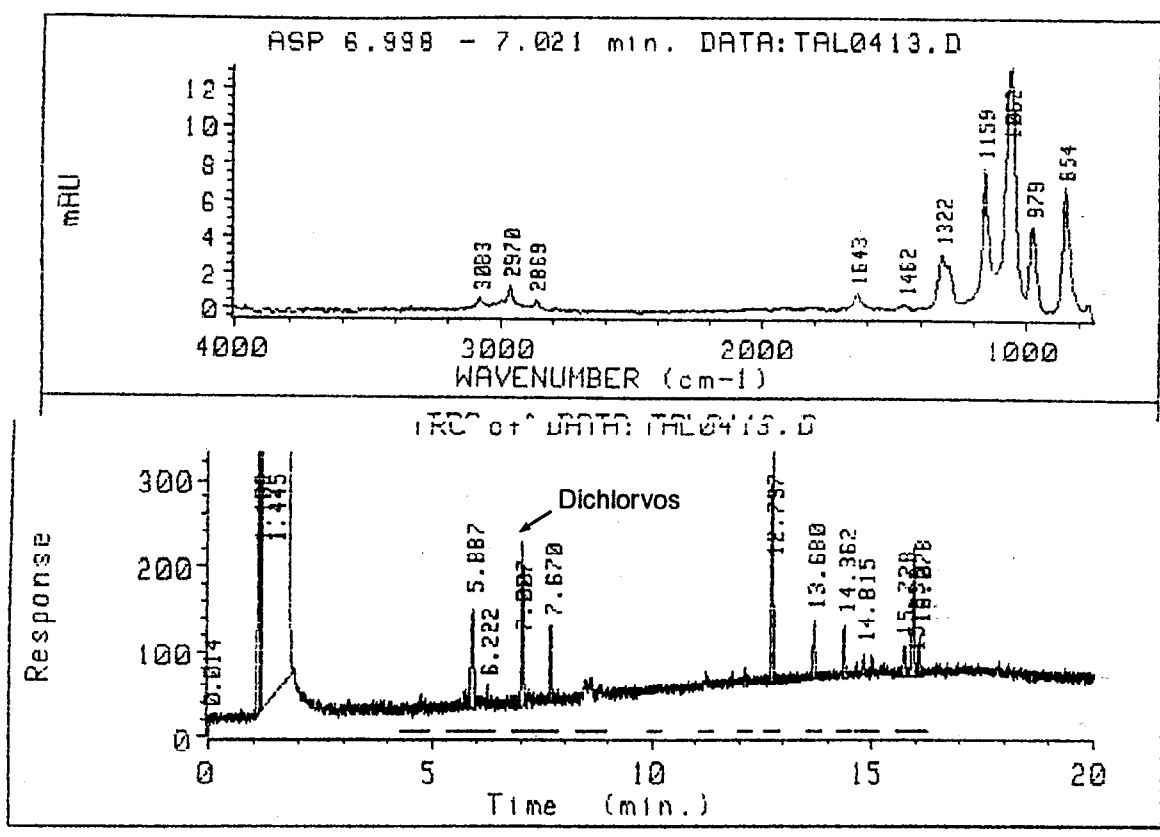
DIBROM	
000500-76-5	757
GARDONA. RABON. TE	930
DICHOXVOS	
000062-73-7	923
PROPYL DISULFIDE	
000629-19-6	907
5(1-HYDROXYHEXYL)-1-H	904
5(1-HYDROXYPROPYL)-1	891
PHOSPHOROTHIOIC ACID	
000122-14-5	864



Infrared Spectrum
from Sample
Injected

Infrared Spectrum
from Library Search

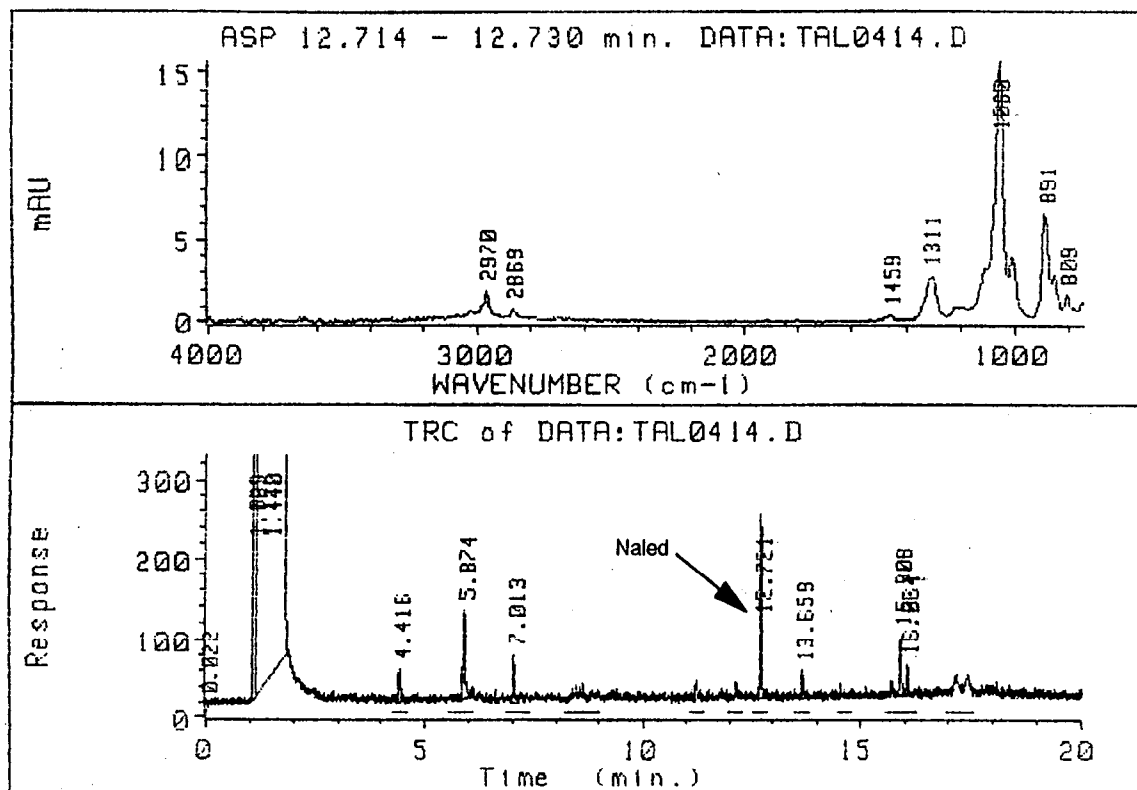
Figure 11. FTIR Confirmation: Log 35 - 6N, Dichlorvos



← Infrared Spectrum
from Sample
Injected

← Infrared Spectrum
from Library Search

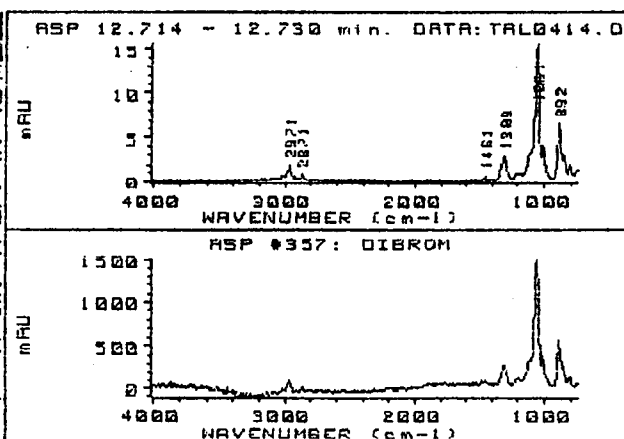
Figure 12. FTIR Confirmation: Sample Log 9 - 1N, Naled



GRAPHICS RESULTS

Version 1.0 25-Feb-87

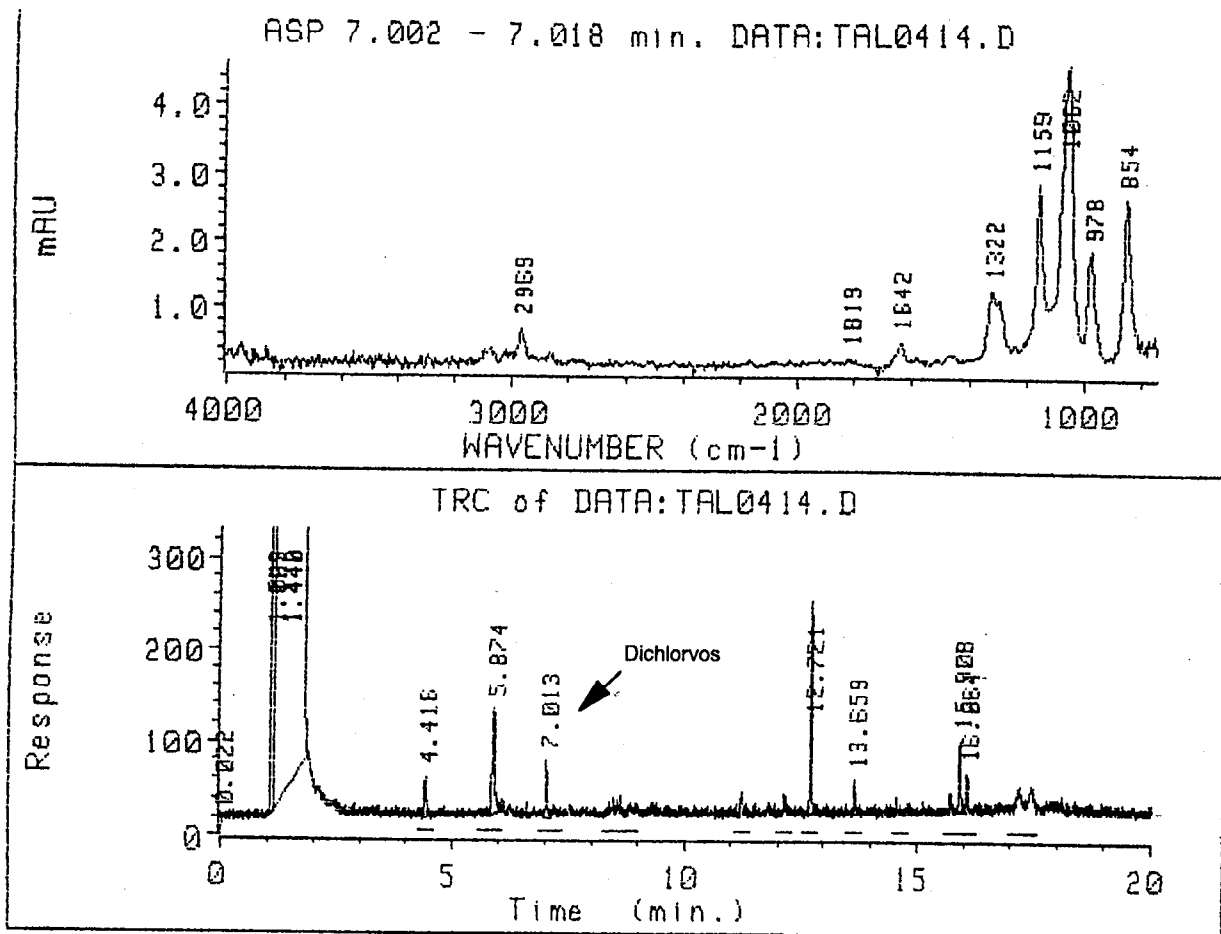
DIBROM	957
000000-72-5	957
GARDONR. RABON. TE	929
DICHOXYDS	922
000062-73-7	922
PROPYL DISULFIDE	907
000629-19-6	907
5(1-HYDROXYHEXYL)-1-N	904
5(1-HYDROXYPROPYL)-1	892
PHOSPHOROTHIOIC ACID	864
000122-14-5	864



← Infrared Spectrum from Naled Injected

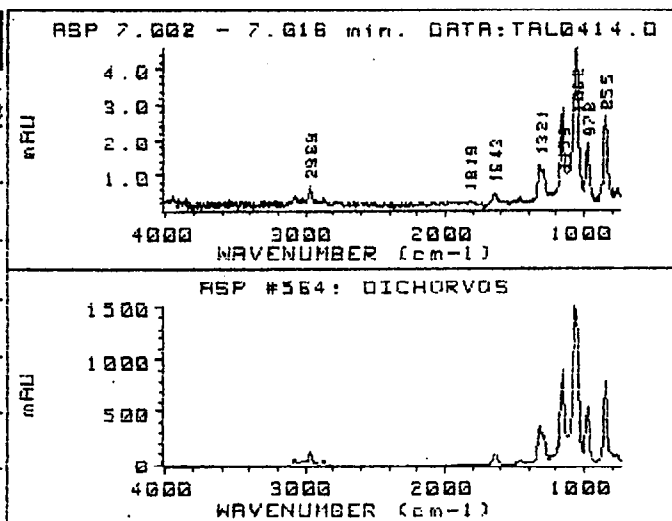
← Infrared Spectrum from Library Search

Figure 13. FTIR Confirmation: Sample Log 9 - 1N, Dichlorvos



GRAPHICAL RESULTS

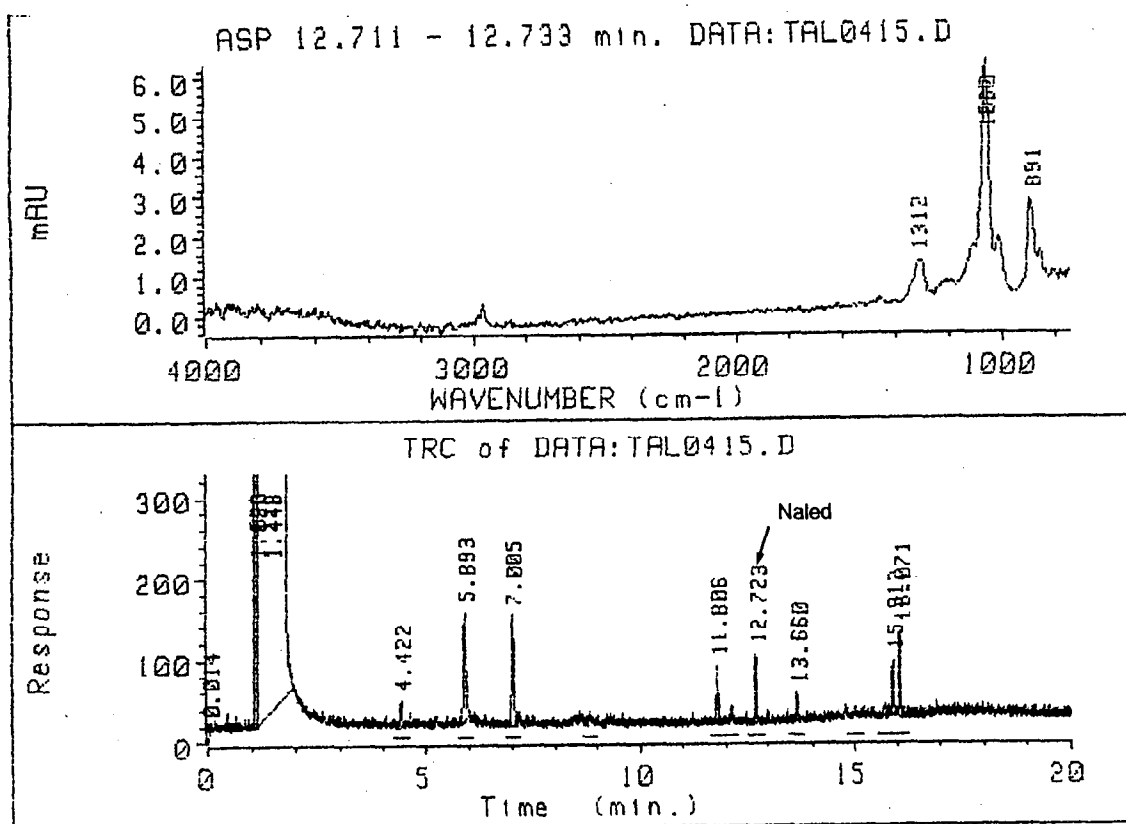
DICHLORVOS
000062-73-7 751
NAPHTHALENE, 1-ETHYL
001127-76-0 833



← Infrared Spectrum
from Naled Injected

← Infrared Spectrum
from Library Search

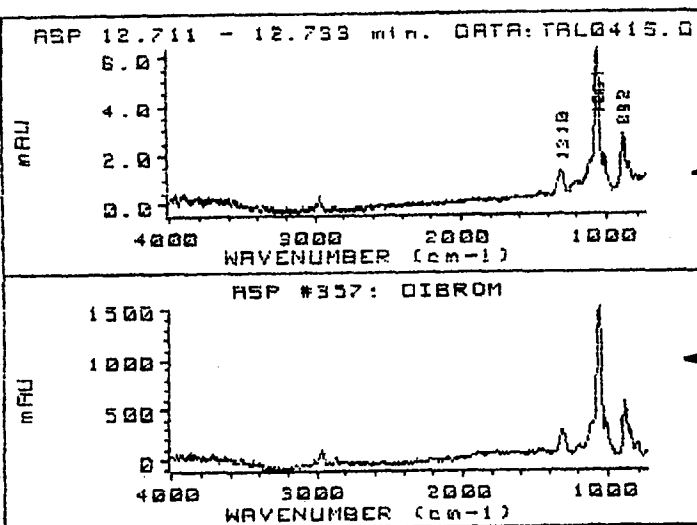
Figure 14. Fortified XAD-4 Resin @ 20 µg Naled and Dichlorvos, Naled Spectrum



GRAPHICS RESULTS

Version 1.0 25-Feb-87

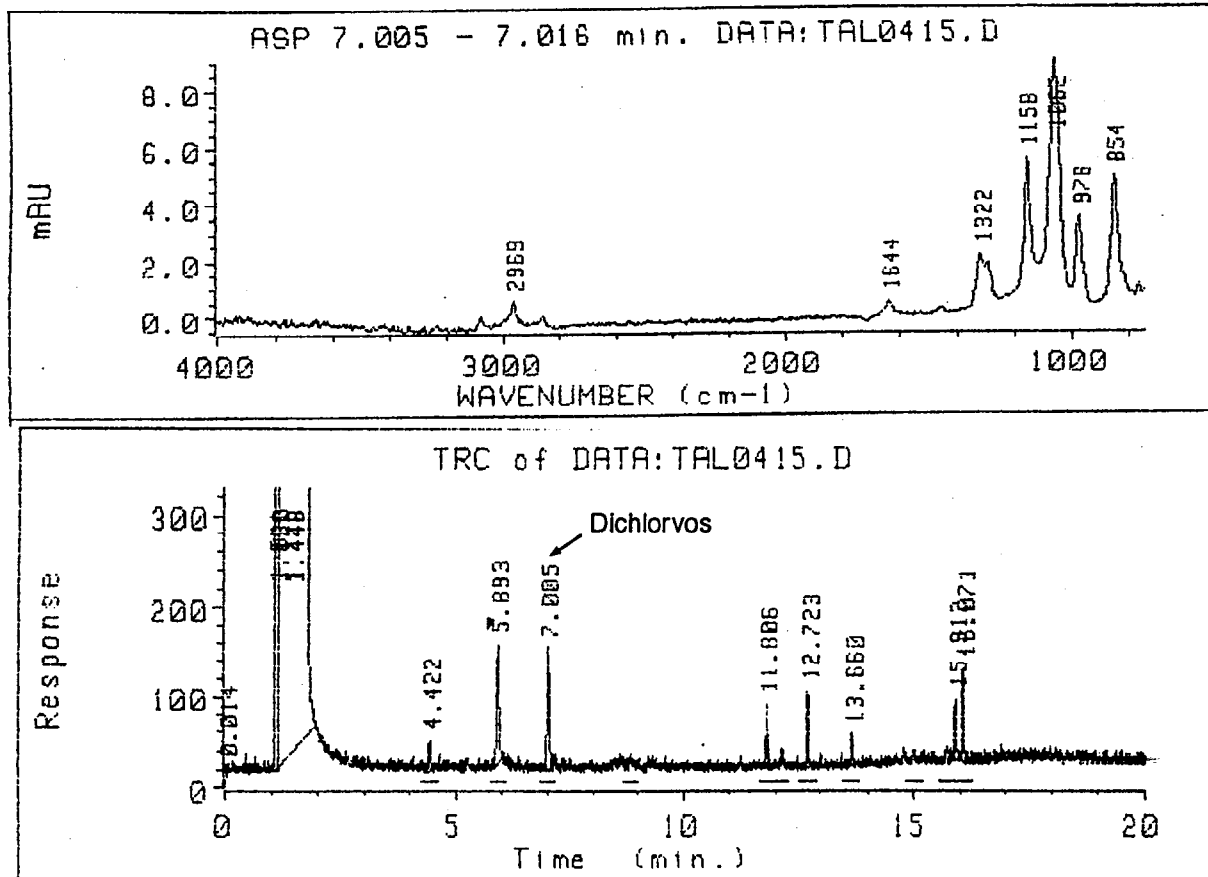
DIBROM
000300-76-5 944
GARDONA. RABON. TE
915
PROPYL DISULFIDE
000629-19-6 895
MONOCROTOPHOS. AZDDR
006923-22-4 892
5(1-HYDROXYHEXYL)-1-H
891
1-NAPHTHALDEHYDE
000066-77-3 877
5(1-HYDROXYPROPYL)-1
669
FENITROTHION
000122-14-5 864
BARBAN
000101-27-9 861



← Infrared Spectrum
from Sample
Injected

← Infrared Spectrum
from Library Search

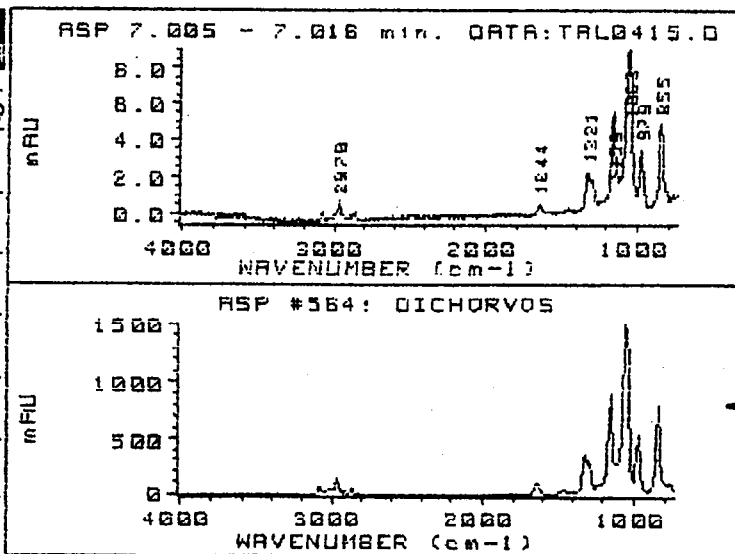
Figure 15. Fortified XAD-4 Resin @ 20 µg Naled and Dichlorvos, Dichlorvos Spectrum



GRAPHICS RESULTS

Version 1.0 25-Feb-87

DICHLORVOS
000062-73-7 774
NAPHTHALENE, 1-ETHYL
001127-76-0 849



← Infrared Spectrum
from Sample
Injected

← Infrared Spectrum
from Library Search

APPENDIX II.
SAMPLING PROTOCOL

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Application Monitoring of Naled During Summer, 1995

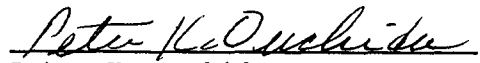
Engineering and Laboratory Branch
Monitoring and Laboratory Division


Project No. C91-031A

Date: April 19, 1995

APPROVED:


Don Fitzell, Project Engineer


Peter K. Ouchida, Manager
Testing Section


George Lew, Chief
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for Naled Monitoring During Summer, 1995

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will conduct source impacted application site monitoring for naled (dibrom) and its major breakdown product, dichlorvos (DDVP). The monitoring is in support of the DPR toxic air contaminant program. Section 14022(c) of the Food and Agriculture Code requires the ARB "to document the level of airborne emissions of pesticides which may be determined to pose a present or potential hazard..." when requested by the Department of Pesticide Regulation. This monitoring will be conducted near a specific application, prior to, during, and following an application of this pesticide. Naled is an organophosphate ester insecticide used on numerous crops often within four days of harvest.

II. Sampling

Calibrated rotometers will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling media, XAD-4 resin, installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field size, application rate, formulation, method of application and length of application.

Prior to application, background samples will be taken to establish if any naled or dichlorvos is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with XAD resin using battery powered pumps capable of flows of approximately 15 liters per minute (ATTACHMENT I). Four samplers will be used; one on each side (assuming a rectangular field) of the field at a distance of approximately 15 yards. These distances are approximate and dependent on the physical obstacles surrounding the field. As closely as feasible, the sample tubes will be changed according to the schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT II).

III. Analysis

The analysis will be conducted under contract by staff at the Trace Analysis Laboratory, Department of Environmental Toxicology, UC Davis. All samples will be stored in an ice chest containing dry ice or a freezer until analysis. Samples will be extracted with 50 ml of ethyl acetate and analyzed using a gas chromatograph. The column is a 15 meter Megabore DB-5. Quantitation will be by a nitrogen/phosphorus detector. If required, a clean up procedure using a

silicic acid column has been developed. The (S.O.P.) for the analysis of naled and dichlorvos will be included in the final report.

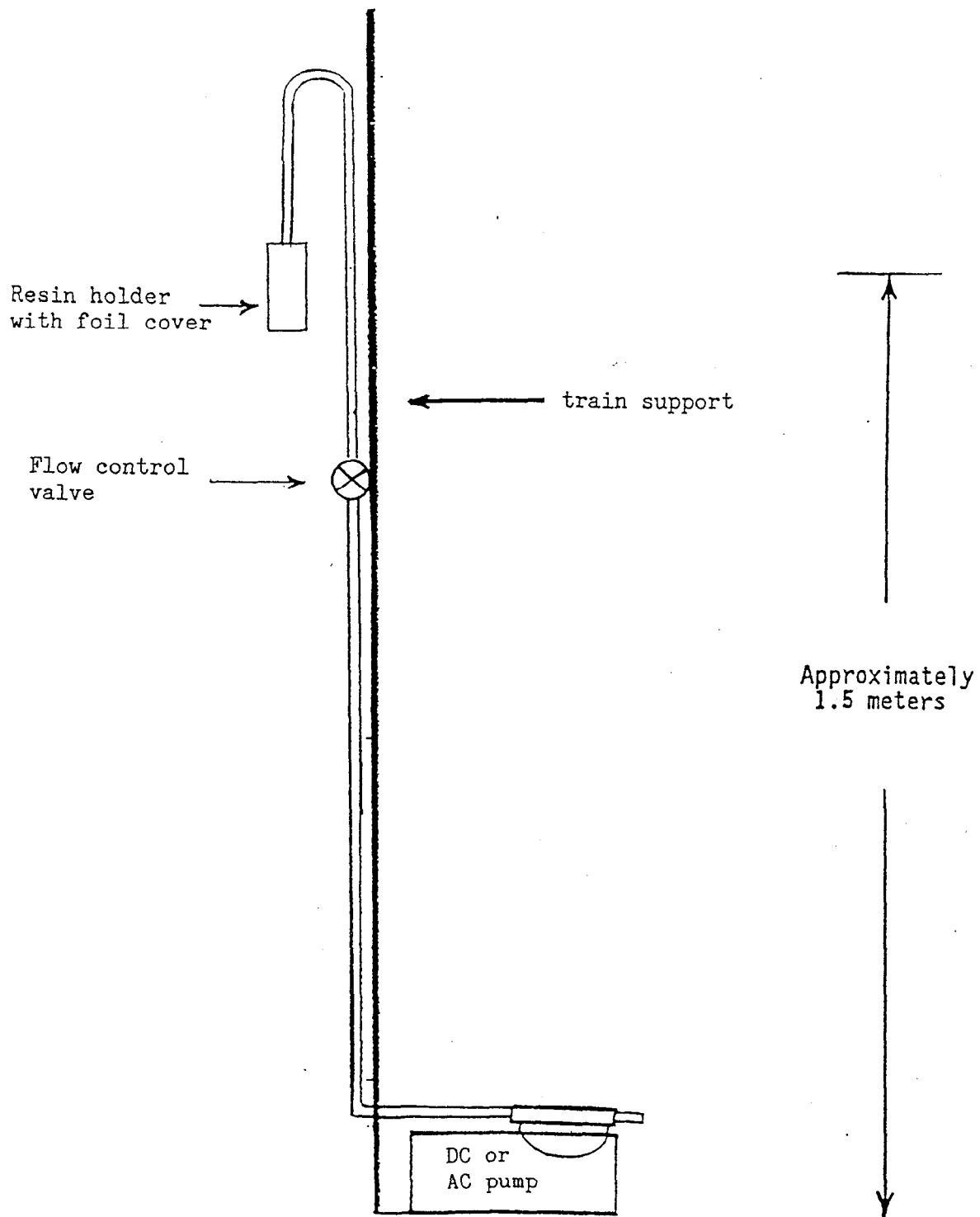
IV. Quality Assurance

Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring." The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Sample flow rates will be calibrated prior to and after sampling in the field.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and an Instrument Technician.

ATTACHMENT I
PESTICIDE MONITORING APPARATUS



ATTACHMENT II
QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN
FOR PESTICIDE MONITORING

Prepared by the
Monitoring and Laboratory Division
and
Stationary Source Division

Revised: February 4, 1994

APPROVED:

Geri Shum, Chief
Toxic Air Contaminant
Identification Branch

W. P. Cook, Chief
Quality Management and Operations
Support Branch

George Lee, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

<u>Height Above Ground (Meters)</u>	<u>Minimum Distance From Supporting Structure (Meters)</u>		<u>Other Spacing Criteria</u>
	<u>Vertical</u>	<u>Horizontal</u>	
2-15	1	1	<ol style="list-style-type: none"> 1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as $\mu\text{g}/\text{m}^3$ (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX III.
PORTERVILLE AIRPORT WEATHER DATA

PORTERVILLE AIRPORT DATA

From 6/5/95 - 6/9/95

Site	Time	Cloud Cover	Visibility (mi)	Temp (F)	Dew pt (F)	Wind Direction	Speed (Knots)
6/5/95							
PTV SA	0054	Clear	10	65	47	300	7
PTV SA	0154	Clear	10	63	48	340	8
PTV SA	0254	Clear	10	60	47	310	5
PTV SA	0354	Clear	10	57	47	280	3
PTV SA	0454	Clear	10	55	47	180	5
PTV SA	0554	Clear	10	53	47	200	4
PTV SA	0654	Clear	10	57	49	290	6
PTV SA	0754	Broken	10	61	49	300	9
PTV SA	0854	Overcast	10	61	49	320	12
PTV SA	0954	Overcast	10	63	49	340	9
PTV SA	1054	Overcast	10	66	48	350	10-16
PTV SA	1154	Scattered	10	70	48	30	6
PTV SA	1254	Scattered	10	73	44	340	10-17
PTV SA	1354	Scattered	10	76	46	320	14-26
PTV SA	1454	Clear	10	76	41	330	14-21
PTV SA	1554	Clear	10	76	36	320	14-23
PTV SA	1654	Clear	10	76	36	330	14-21
PTV SA	1754	Clear	10	75	35	330	15
PTV SA	1854	Clear	10	73	34	320	16-21
PTV SA	1954	Clear	10	70	35	310	7
PTV SA	2054	Clear	10	66	34	320	9
PTV SA	2154	Clear	10	61	33	310	5
PTV SA	2254	Clear	10	60	34	0	0
PTV SA	2354	Clear	10	53	38	220	4
6/6/95							
PTV SA	0054	Clear	10	49	37	120	5
PTV SA	0154	Clear	10	49	37	210	4
PTV SA	0254	Clear	10	47	37	160	5
PTV SA	0354	Clear	10	46	37	150	5
PTV SA	0454	Clear	10	45	36	140	7
PTV SA	0554	Clear	10	45	36	160	6
PTV SA	0654	Clear	10	50	38	160	5
PTV SA	0754	Clear	10	55	41	280	3
PTV SA	0854	Clear	10	58	42	170	4
PTV SA	0954	Clear	10	62	42	0	0
PTV SA	1054 (a)	Clear	10	64	43	0	0
PTV SA	1154	Clear	10	66	43	0	0
PTV SA	1254	Clear	10	69	43	320	8
PTV SA	1354	Clear	10	73	42	350	12-17
PTV SA	1454	Clear	10	75	36	330	13-21
PTV SA	1554	Clear	10	76	34	350	13-20
PTV SA	1654	Clear	10	75	30	330	13-21
PTV SA	1754	Clear	10	74	29	340	14-20
PTV SA	1854	Broken	10	71	28	320	16
PTV SA	1954	Clear	10	69	28	330	14-20
PTV SA	2054	Clear	10	64	27	310	8
PTV SA	2154	Clear	10	60	31	280	5
PTV SA	2254	Clear	10	59	33	0	0
PTV SA	2354	Clear	10	57	33	0	0

PORTERVILLE AIRPORT DATA

From 6/5/95 - 6/9/95

Site	Time	Cloud Cover	Visibility (mi)	Temp (F)	Dew pt (F)	Wind Direction	Speed (Knots)
6/7/95							
PTV SA	0054	Clear	10	51	35	170	7
PTV SA	0154	Clear	10	48	35	150	4
PTV SA	0254	Clear	10	47	34	130	3
PTV SA	0354	Clear	10	47	34	150	6
PTV SA	0454	Clear	10	46	33	160	7
PTV SA	0554 (a)	Clear	10	49	34	170	8
PTV SA	0654	Clear	10	51	34	170	9
PTV SA	0754 (a)	Clear	10	56	35	230	7
PTV SA	0854	Clear	10	61	36	290	5
PTV SA	0954	Clear	10	61	35	200	3
PTV SA	1054	Scattered	10	63	35	260	5
PTV SA	1154	Scattered	10	65	35	250	6-14
PTV SA	1254	Scattered	10	67	35	270	10
PTV SA	1354	Broken	10	66	35	290	7
FAT SA	1450 (b)	Broken	10	71	33	220	4
FAT SA	1550 (b)	Overcast	10	70	34	330	8
FAT SA	1650 (b)	Overcast	10	68	36	70	17-22
PTV SA	1754	Clear	10	68	37	320	4
PTV SA	1854	Clear	10	67	39	250	6
PTV SA	1954	Clear	10	63	39	220	6
PTV SA	2054	Clear	10	58	39	200	7
PTV SA	2154	Clear	10	53	39	120	6
PTV SA	2254	Clear	10	52	39	130	6
PTV SA	2354	Clear	10	53	37	110	5
6/8/95							
PTV SA	0054	Clear	10	51	36	120	6
PTV SA	0154	Clear	10	49	37	110	8
PTV SA	0254	Clear	10	50	36	110	5
PTV SA	0354	Clear	10	50	36	110	6
PTV SA	0454	Clear	10	50	36	120	6
PTV SA	0554 (a)	Clear	10	54	37	110	6
PTV SA	0654	Clear	10	57	37	110	6
PTV SA	0754	Clear	10	62	38	100	5
PTV SA	0854	Clear	10	64	37	200	5
PTV SA	0954	Clear	10	68	38	0	0
PTV SA	1054	Clear	10	70	37	310	5
PTV SA	1154	Clear	10	72	38	290	5
PTV SA	1254	Clear	10	75	38	350	5
PTV SA	1354	Clear	10	75	37	300	8
PTV SA	1454	Clear	10	77	38	300	9
PTV SA	1554	Clear	10	79	37	300	11-15
PTV SA	1654	Clear	10	78	35	310	6
PTV SA	1754	Clear	10	78	34	310	9
PTV SA	1854	Clear	10	77	36	340	8
PTV SA	1954	Clear	10	73	37	320	6
PTV SA	2054	Clear	10	71	39	20	4
PTV SA	2154	Clear	10	62	41	0	0
PTV SA	2254	Clear	10	62	39	100	5
PTV SA	2354	Clear	10	59	38	200	5

PORTERVILLE AIRPORT DATA

From 6/5/95 - 6/9/95

Site	Time	Cloud Cover	Visibility (mi)	Temp (F)	Dew pt (F)	Wind Direction	Speed (Knots)
6/9/95							
PTV SA	0054	Clear	10	57	38	120	4
PTV SA	0154	Clear	10	54	40	130	4
PTV SA	0254	Clear	10	53	39	150	5
PTV SA	0354	Clear	10	51	39	150	4
PTV SA	0454	Clear	10	52	38	180	7
PTV SA	0554 (a)	Clear	10	53	39	160	6
PTV SA	0654	Clear	10	54	40	150	5
VIS SA	0754 (c)	Clear	10	59	44	140	4
VIS SA	0854 (d)	Clear	10	63	47	140	4
PTV SA	0954	Clear	10	70	42	230	6
PTV SA	1054	Clear	10	73	43	220	9
PTV SA	1154	Clear	10	75	44	230	6
PTV SA	1254	Clear	10	78	45	270	4
PTV SA	1354	Clear	10	80	41	290	5
PTV SA	1454	Clear	10	81	43	280	8
PTV SA	1554	Clear	10	83	42	320	5
PTV SA	1654	Clear	10	84	43	310	9
PTV SA	1754	Clear	10	83	42	330	7
PTV SA	1854	Clear	10	82	42	320	6
PTV SA	1954	Clear	10	78	43	310	6
PTV SA	2054	Clear	10	72	47	310	3
PTV SA	2154	Clear	10	68	46	0	0
PTV SA	2254	Clear	10	63	47	120	3
PTV SA	2354	Clear	10	61	46	120	4

Key:

Time = Pacific Daylight-Savings Time

- (a) Porterville Airport data was averaged (the hour before and the hour after) when one hour of data was missing.
- (b) Fresno Airport data was substituted when neither Porterville Airport data, or Visalia Airport data was available for more than one hour.
- (c) Porterville and Visalia Airport data was combined and averaged.
- (d) Visalia Airport data was substituted and averaged when more than one hour of data was missing.

APPENDIX IV.
QMOSB AUDIT REPORT

7'
STATE OF CALIFORNIA

AIR RESOURCES BOARD

AUDIT REPORT

NALED MONITORING IN THE SAN JOAQUIN VALLEY

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

SEPTEMBER 1995

AUDIT REPORT
NALED MONITORING IN THE SAN JOAQUIN VALLEY

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ATTACHMENTS

- I. Flow Rate Audit Procedures for Air Samplers Used in Pesticide Monitoring
- II. Performance Audit Procedures for the Laboratory Analysis of Naled and Its Breakdown Product Dichlorvos

LIST OF FIGURES

1. Air Sampler Used in the Monitoring of Naled

I. EXECUTIVE SUMMARY

In June 1995, the Engineering and Laboratory Branch of the California Air Resources Board conducted ambient air sampling in the San Joaquin Valley of California to document the airborne emissions of naled and its breakdown product, dichlorvos, in the vicinity of a treated field during and after an application. The samples were collected by the Engineering and Laboratory Branch and analyzed by the Trace Analytical Laboratory of the UC Davis Department of Environmental Toxicology.

The California Air Resources Board Monitoring and Laboratory Division's Quality Assurance Section staff conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (California Air Resources Board, February 4, 1994).

Additionally, Quality Assurance Section staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The difference between the reported and assigned flow rates averaged 1.3% with a range of -0.7% to 5.0%. In order to determine the effectiveness of the analytical procedure, laboratory performance audits were also conducted. On June 2, 1995, twenty two samples spiked with measured amounts of naled and dichlorvos were submitted to the laboratory for analysis. The samples were prepared from naled and dichlorvos standard solutions obtained from Chem Service. Of the twenty two samples submitted for analysis, seven were spiked with naled only, seven were spiked with dichlorvos only, eight were spiked with both naled and dichlorvos, and there was one blank. The difference between the assigned and the reported total mass of the naled samples averaged 4.8% with a range of -6.0% to 14.4%. The difference between the assigned and the reported total mass of the dichlorvos samples averaged -1.6% with a range of -12.0% to 8.0%. The difference between the assigned and the reported total mass of the combined naled/dichlorvos samples averaged 1.4% with a range of -1.6% to 6.4%. There was a 0.0% difference between the assigned and the reported mass for the blank sample.

II. CONCLUSIONS

The records for field operations, sample handling and storage procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring. The results of the reported flow rates were in good agreement with the actual flow rates measured by Quality Assurance Section staff. The results of the analytical performance audit showed an average of 4.8% difference for naled, -1.6% difference for dichlorvos, and 1.4% difference for the combined naled/dichlorvos samples.

III. RECOMMENDATIONS

There are no recommendations at this time.

IV. INTRODUCTION

In June 1995, the Engineering and Laboratory Branch (ELB) of the California Air Resources Board (CARB) conducted ambient air sampling in the San Joaquin Valley of California to document the airborne emissions of naled and its breakdown product, dichlorvos, in the vicinity of a treated field during and after an application. The samples were collected by the ELB and analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology. The CARB Monitoring and Laboratory Division (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers' flow rates and of the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (CARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in July 1995 through a questionnaire submitted to TAL staff. The protocol for ambient air monitoring of naled and the laboratory sampling methodology for the analysis of naled and dichlorvos were also reviewed. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through a Teflon holder containing 30 ml of cleaned XAD-4 resin. The air samplers consisted of one sample holder, connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). The samplers' rotameters were set to an indicated flow rate of 15 liters per minute (lpm) by adjusting the control valve on the rotameter.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the XAD-4 resin was removed from the Teflon holder and transferred into a glass jar with a Teflon-lined lid. The jars were stored in an ice chest containing dry ice. During shipment, the samples were boxed, placed in a plastic cooler with dry ice, and wrapped with duct tape. Samples were stored in the field for up to two days prior to shipment and were determined to be stable for at least 30 days.

Upon receipt at the laboratory, the samples were stored in a freezer for a maximum of two days until extraction and analyses were conducted.

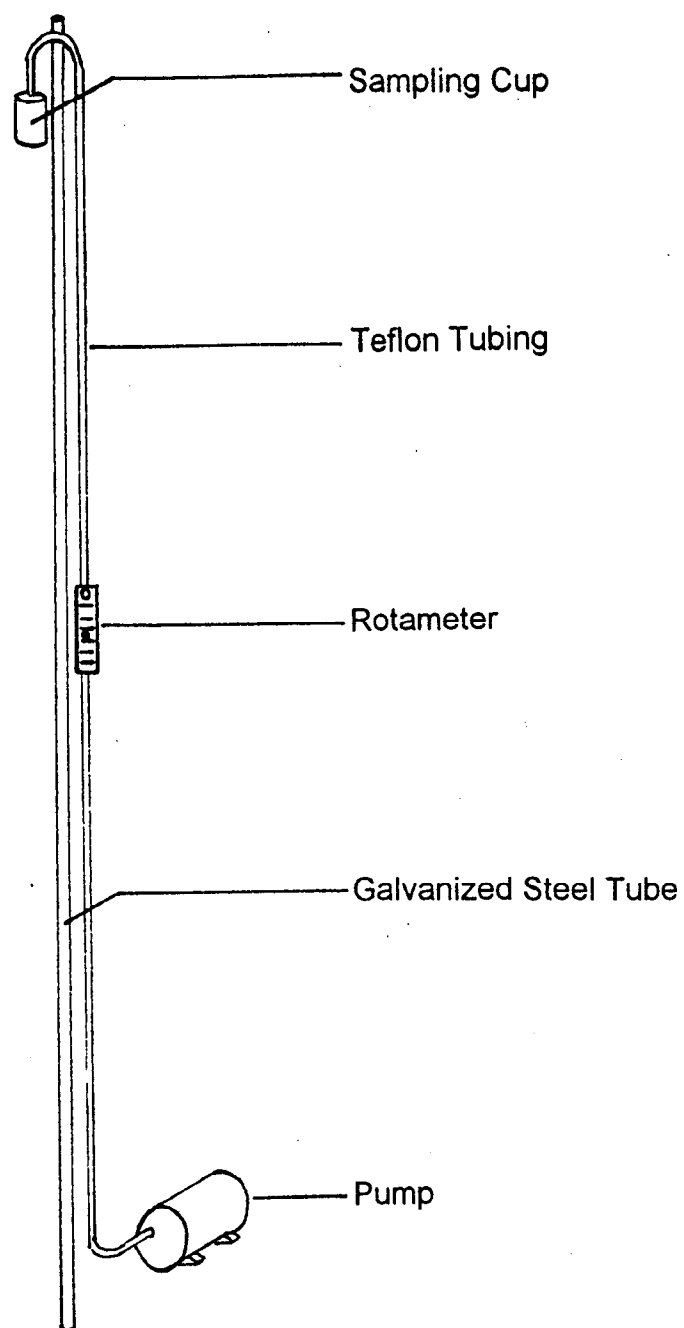


Figure 1. Air sampler used in the monitoring of naled.

Sample Analysis

The analytical method was developed by the TAL, and is described below. The samples were swirled in ethyl acetate for one-half hour. One-half of the sample was put away for future use, if necessary. The other half was stripped of solvent and the sample was transferred and made to a final volume of 3 ml. The samples were analyzed using a Hewlett Packard Model 5890 Gas Chromatograph (GC) with a nitrogen-phosphorus detector.

Quality control activities performed to monitor and document the quality of the data included analysis of a field control blank with every sample set and laboratory spikes of three replicates per set of samples with 107% \pm 11.3% recovery for naled and 107% \pm 6.6% recovery for dichlorvos. Field duplicates from collocated sites were collected once each sampling day. A portion of the samples was analyzed by GC/Mass Spectroscopy Selective Ion monitoring and FT/IR to confirm the identity of the analyte.

Method Validation

The limit of detection (LOD) was determined by injecting known quantities of external standards into a GC. The LOD was calculated as the (minimum amount of standard/volume) + total sample volume. Trapping efficiency was determined as >95% for dichlorvos and >75% for naled. The laboratory trapping efficiency study conditions differed from field conditions in that the field air flow was approximately 1/4 of the rate used to determine trapping efficiency. Also, for trapping efficiencies, primary and backup traps were used. Backup traps were not used for the application site samples. Sample stability studies were conducted which verified the integrity of the sample to be 103% \pm 8.15% for naled and 110% \pm 6.0% for dichlorvos. Samples are stable for at least 30 days. Breakthrough mass load was 100 ug over 24 hours at a flow rate of 50 lpm, and the detection limit value was 0.030 ug/sample for both naled and dichlorvos.

Documentation

All samples received by the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were received by the TAL. The information recorded on the field data sheets included sampling date, log number, identification number, description, job name, date, job number, and initials of the field technician.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, date of analysis, results of analysis, and analyst.

The raw data are available for review and electronic files are kept for four years.

VII. PERFORMANCE AUDITS

Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on May 8, 1995, following the procedures outlined in Attachment I. The audit was conducted with a 0 to 30 lpm mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged 1.3% and ranged from -0.7% to 5.0% (Table 1).

Table 1. Results of the flow rate audit of the samplers used in the monitoring of naled.

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1	14.8	14.1	5.0
2	14.8	14.6	1.4
3	14.8	14.9	-0.7
4	14.8	14.9	-0.7
5	14.8	14.5	2.1
6	14.8	14.7	0.7

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

Laboratory Performance Audit

The accuracy of the analytical method was evaluated by submitting for analysis a set of twenty two audit samples spiked with measured amounts of naled and dichlorvos. The samples were prepared by QAS staff on June 2, 1995, following the procedures outlined in Attachment II. The audit samples were extracted and analyzed on June 9. The difference between the assigned and the reported total mass of the naled samples averaged 4.8% with a range of -6.0% to 14.4% (Table 2). For the naled samples, the laboratory also included the amount of dichlorvos present in the sample. The reason for this is that typically, roughly 4-5% of a naled analytical standard is actually dichlorvos. Therefore, any sample spiked with naled, with or without dichlorvos, will have biased dichlorvos results. The amount of dichlorvos present in the samples was not greater than 0.1 ug so it was not included in the determination of the average percent difference for naled samples.

The difference between the assigned and the reported total mass of the dichlorvos samples averaged -1.6% with a range of -12.0% to 8.0% (Table 3). Samples containing both naled and dichlorvos had an average difference of 1.4% with a range of -1.6% to 6.4% between the assigned and the reported total mass (Table 4). The percent difference for the blank sample was not included in the calculations of the average percent differences for the samples.

Table 2. Results of analyses of the naled samples.

SAMPLE ID	ASSIGNED VALUE (ug)	REPORTED VALUE (UG)		PERCENT DIFFERENCE
	NALED	NALED	DICHLORVOS*	
=====				
NAL-2	0.50	0.53	<0.03	6.00
NAL-5	1.25	1.31	0.04	4.80
NAL-8	2.50	2.55	0.09	2.00
NAL-13	0.50	0.47	<0.03	-6.00
NAL-15	1.25	1.38	0.05	14.40
NAL-17	2.50	2.67	0.08	6.80
NAL-22	1.25	1.32	0.06	5.60

* Not included in the determination of percent difference. Signifies dichlorvos present in naled standard.

Table 3. Results of the analyses of the dichlorvos samples.

SAMPLE ID	ASSIGNED VALUE (ug) DICHLORVOS	REPORTED VALUE (UG) DICHLORVOS	PERCENT DIFFERENCE
=====			
NAL-1	0.63	0.57	- 9.52
NAL-3	2.50	2.54	1.60
NAL-4	0.25	0.22	-12.00
NAL-10	0.25	0.25	0.00
NAL-12	0.63	0.62	- 1.59
NAL-19	0.25	0.27	8.00
NAL-21	2.50	2.55	2.00

Table 4. Results of analyses of the naled/dichlorvos samples.

SAMPLE ID	ASSIGNED VALUE (ug)		REPORTED VALUE (UG)		PERCENT DIFFERENCE
	NALED	DICHLORVOS	NALED	DICHLORVOS	
NAL-6	0.50	0.25	0.49	0.26	0.00
NAL-7	5.00	1.25	4.81	1.42	-0.32
NAL-9	1.25	0.63	1.24	0.61	-1.60
NAL-11	5.00	1.25	4.79	1.48	0.32
NAL-14	0.50	0.25	0.49	0.26	0.00
NAL-16	1.25	0.63	1.36	0.64	6.38
NAL-18*	0.00	0.00	0.00	0.00	0.00
NAL-20	0.50	0.25	0.52	0.27	5.33

* Not included in the determination of average percent difference.

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

ATTACHMENT I

Flow Rate Audit Procedures for Air Samplers
Used in Pesticide MonitoringIntroduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter standardized against a NIST-traceable flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedures for the Laboratory Analysis of Naled and Its Breakdown Product Dichlorvos

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory to measure the ambient concentrations of naled and dichlorvos. The audit is conducted by submitting audit samples spiked with known concentrations of naled and dichlorvos. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Naled, 0.05 ug/ul in ethyl acetate, Chem Service, Lot # 154-17B
2. Dichlorvos, 0.025 ug/ul in ethyl acetate, Chem Service, Lot # 154-17A
3. Glass jars with Teflon-lined lids, 30 ml XAD-4 resin

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of Audit Samples

Prepare twenty two audit samples by spiking the XAD-4 resin contained in the glass jars with the volume of naled/dichlorvos solution indicated in Table 1, below. Using a microsyringe, slowly expel the solution into the glass jar, move the syringe so that the solution is not landing in the same place on the resin. Touch the tip of the syringe to the side of the glass jar to expel the last bit of solution.

Table 1: Volume of Naled/Dichlorvos Used to Spike Audit Samples

Sample ID	Naled Spiking Solution (ul)	Dichlorvos Spiking Solution (ul)	Total Spiking Solution (ul)
NAL-1	0	25	25
NAL-2	10	0	10
NAL-3	0	100	100
NAL-4	0	10	10
NAL-5	25	0	25
NAL-6	10	10	20
NAL-7	100	50	150
NAL-8	50	0	50
NAL-9	25	25	50
NAL-10	0	10	10
NAL-11	100	50	150
NAL-12	0	25	25
NAL-13	10	0	10
NAL-14	10	10	20
NAL-15	25	0	25
NAL-16	25	25	50
NAL-17	50	0	50
NAL-18	0	0	0
NAL-19	0	10	10
NAL-20	10	10	20
NAL-21	0	100	100
NAL-22	25	0	25